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ORGANIC MATTER IN ANOXIC PORE WATER FROM GREAT BAY, NEW HAMPSHIRE

WILLIAM HENRY OREM V.

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University of New Hampshire PH.D. 1982

ORGANIC MATTER IN ANOXIC PORE WATER FROM GREAT BAY, NEW HAMPSHIRE

BY

William Henry Orem, V
B.S., Lehigh University
M.S., University of Delaware

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy
in
Chemistry

May, 1982

This dissertation has been examined and approved.

Dissertation director, Henri E. Gaudette
Professor of Earth Sciences

N. Dennis Chasteen, Professor of Chemistry

C.L. Grant, Professor of Chemistry

Paul R. Jones, Professor of Chemistry

W. Berry Lyons, Assistant Professor of Earth Sciences

May 10, 1982
Date

DEDICATION

This dissertation is dedicated to my parents, Don and Helyn Orem, whose love, understanding and support when I needed it most has helped me complete this work and make it through life so far.

'Ars longa, vita brevis'

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Mark Hines gets a paragraph of his own in thanks for his support, help and interest in this project; thanks also Mark for the moral support

during the low times. I think we may very well have solved it all in Milwaukee.

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ABSTRACT

ORGANIC MATTER IN ANOXIC PORE WATER
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University of New Hampshire, May, 1982

A complete understanding of the anaerobic decomposition of organic matter in marine sediments is desirable for two reasons: 1) the life processes of sulphate reducing bacteria result in the production of a number of byproducts (e.g. reduced sulphur compounds), which affect diagenetic reactions, most notably those influencing the mobility of trace metals in the environment, and 2) changes in the character of organic matter resulting from anaerobic decomposition may be important in the later formation of large organic polymers such as humic acid, kerogen and petroleum. Studies of organic species in pore water often provide information on diagenetic processes unavailable from work on sedimentary organic matter, since variations in pore water composition are much more sensitive indicators of chemical and biological reactions occurring in this environment. However, few studies of pore water organic matter have been conducted. This work had three major goals: 1) a study of collection and handling techniques for pore water organic, 2) a comprehensive survey of the dissolved organic carbon distribution in Great Bay, N.H. pore waters and 3) an investigation of some of the bulk char-

acteristics of pore water organic matter from Great Bay sediments.

Shallow and deep cores were obtained from a number of sampling sites within the Great Bay Estuary, and pore water obtained by high speed centrifugation of the samples. All sample handling and processing was conducted under oxygen free conditions. It was shown that failure to exclude oxygen from anoxic sediment samples results in changes in both the amounts and nature of the organic matter in the pore water. In addition, the loss of iron, phosphate and titration alkalinity from the pore water of oxygen exposed samples was reaffirmed.

From measured depth profiles of sulphate, ammonia and phosphate in Great Bay pore waters, rates of sulphate reduction and ammonia and phosphate production were calculated using a kinetic model (Berner, 1980). Calculated values of sulphate reduction at two sites in Great Bay agreed quite well with measured rates (Hines, 1981).

Dissolved organic carbon (DOC), in Great Bay pore waters was shown to vary laterally, vertically and seasonally. In surface sediments, the seasonal variation in DOC was coupled to seasonal changes in microbial activities and the bioturbation of marine benthic organisms. In deeper sediments, the seasonal changes in DOC were hypothesized to be coupled to a temperature induce adsorption/desorption mechanism.

The molecular size of pore water organic matter was observed to be relatively large, with the dominant molecular weight range in many cores between 50,000 and 1,000. A method for the fractionation of pore water organic matter using reversed phase high pressure liquid chromatography was developed, and the usefullness of this technique for qualitative studies of this material was demonstrated.

CHAPTER I

INTRODUCTION

I. Scope of Organic Geochemistry

The subject of this dissertation, the biogeochemistry of organic compounds in nearshore anoxic marine sediments, falls under the realm of organic geochemistry. Organic geochemistry is a relatively new scientific discipline which deals with the amounts, origins, transformations and cycling of organic matter in the litho, hydro, bio and atmosphere (Breger, 1963). The beginnings of this field may be traced to the work of Triebs (1934), who isolated a red vanadyl porphyrin complex from crude oil that was structurally similar to the prosthetic group of chlorophyll a. This was a major step forward in the search for the origin of petroleum. Later studies with increasingly more sophisticated analytical methods led to the identification of more of the organic components of petroleum, and the correlation of these structures to those of present-day biological systems. Of particular importance in this regard was the work of Erdman (1961), Bendoraitis et al. (1962), and Cooper and Bray (1963). However, today, nearly 50 years after Triebs' discovery, organic geochemists are still trying to establish the sequence of steps involved in the transformation of detrital biomolecules to geopolymers such as humic substances, kerogen, petroleum and coal. In addition, major gaps exist in our understanding of such fundamental questions as the nature of 90% of the organic matter present in the oceans and sediments (Sharp, 1975; and Gardner and Hanson, 1979), and

the cycling of organic compounds within and between the various geochemical spheres of the earth (Holland, 1978). One major obstacle in the advance of this field has been a lack of proper analytical tools. Perhaps a greater hindrance, however, is the extreme complexity of this system, and our lack of understanding of fundamental processes involving the formation and accumulation of organic matter in the environment.

From a purely analytical viewpoint, the major problem in organic geochemistry is one of separation. A sediment or seawater sample may contain hundreds of thousands or possibly millions of individual organic compounds, and the difficulties involved in separating and identifying the components of this complex mixture must surely be one of the most challenging areas for the application of analytical methods. Reviews of the literature in the areas of petrogenesis (Yen, 1975), and natural products chemistry (Faulkner and Anderson, 1974), illustrate the myriad of individual organic compounds in environmental samples. An additional problem facing the organic geochemist in the analysis of organic matter in seawater and marine sediments is the presence of large concentrations of analytically troublesome inorganic salts in the samples. This is particularly true for marine sediments where, in addition to salts, large quantities of other inorganic substances (e.g. H_2S, NH_3 and CO_2), may interfere with classical methods of analysis. Often, such interferences are difficult to predict a priori, and, indeed, may go unnoticed for many years. Finally, an area of critical importance in environmental chemistry is that of sampling, and manipulation and storage of samples. In organic geochemistry, this applies especially for the analysis of labile or volatile organic compounds, where careless sample manipulation may seriously compromise the integrity of the

sample and the validity of the results obtained. The development of a number of sophisticated analytical methods in the last fifteen years, such as combined gas chromatography-mass spectrometry (GC/MS), (Ettre, 1979), high-resolution nuclear magnetic resonance (NMR), (Hatcher, 1980), reversed phase high performance liquid chromatography (HPLC), (Edwards et al., 1979), and others, has greatly facilitated organic geochemical studies in recent years.

Using these modern analytical techniques, organic geochemists are currently focusing on two major areas of research: 1) elucidating the biogenic pathways involved in the production and decomposition of organic compounds and 2) establishing the distribution and transformations of carbon compounds in soils and sediments. The primary focus of this dissertation has been in this latter area of study, with regard to nearshore marine sediments. However, the oceans are an interactive system, and organic geochemical studies of marine sediments also require information concerning the sources of organic matter and the transformations that change this material prior to its reaching the sediments.

In the past, studies of the diagenesis (e.g. chemical changes), of organic matter in marine sediments have emphasized chemical analysis of the whole sediment (e.g. Degens, 1967; and Hatcher, 1978). While these studies have provided some information, particularly concerning late stages of diagenetic changes in the organic matter, the large amounts of organic matter in nearshore sediments make subtle changes occurring during the early stages of diagenesis difficult to study. For this reason, studies of early diagenesis in recent years have emphasized analyses of chemical species in the pore or interstitial

water of marine sediments (i.e. the seawater present between sediment grains). A schematic illustration of the pore water/sediment system is presented in Figure 1-1. Berner (1974), has described pore waters as an idealized ocean in which chemical reaction rates are maximized. This is a consequence of the large ratio of sediment surface area to pore water volume in natural marine sediments. Thus, the composition of marine pore waters is a sensitive indicator of mineral and microbially mediated diagenetic reactions occurring in the sediments.

II. Sources of Organic Matter to Marine Sediments

All organic matter in the sea originates from primary production. Williams (1971), has estimated that the net input of organic carbon into the oceans is about 3.6×10^{16}g/yr. This input consists of three major sources: 1) net primary production in the sea (3.6×10^{16}g/yr), rain (2.2×10^{14}g/yr), and land runoff (3.1×10^{13}g/yr). Output in this system is primarily via sedimentation, and Williams (1971), has calculated a removal rate of about 9.5×10^{13}g/yr for marine organic matter. Thus, only about 0.3% of the organic carbon entering the sea each year reaches the sediments. These estimates are for the oceans as a whole, and the situation may be somewhat different in the nearshore marine environment where the riverine input is much more important, and the depth of the water column is considerably less (Head, 1976). Indeed, previous work has shown that the majority of the detrital organic matter in estuarine waters is terrestrially derived (Nissenbaum and Kaplan, 1972; Nissenbaum, 1974; and Gardner and Menzel, 1974). Much of this terrestrially derived organic matter is rapidly deposited in estuarine sediments as a result of flocculation

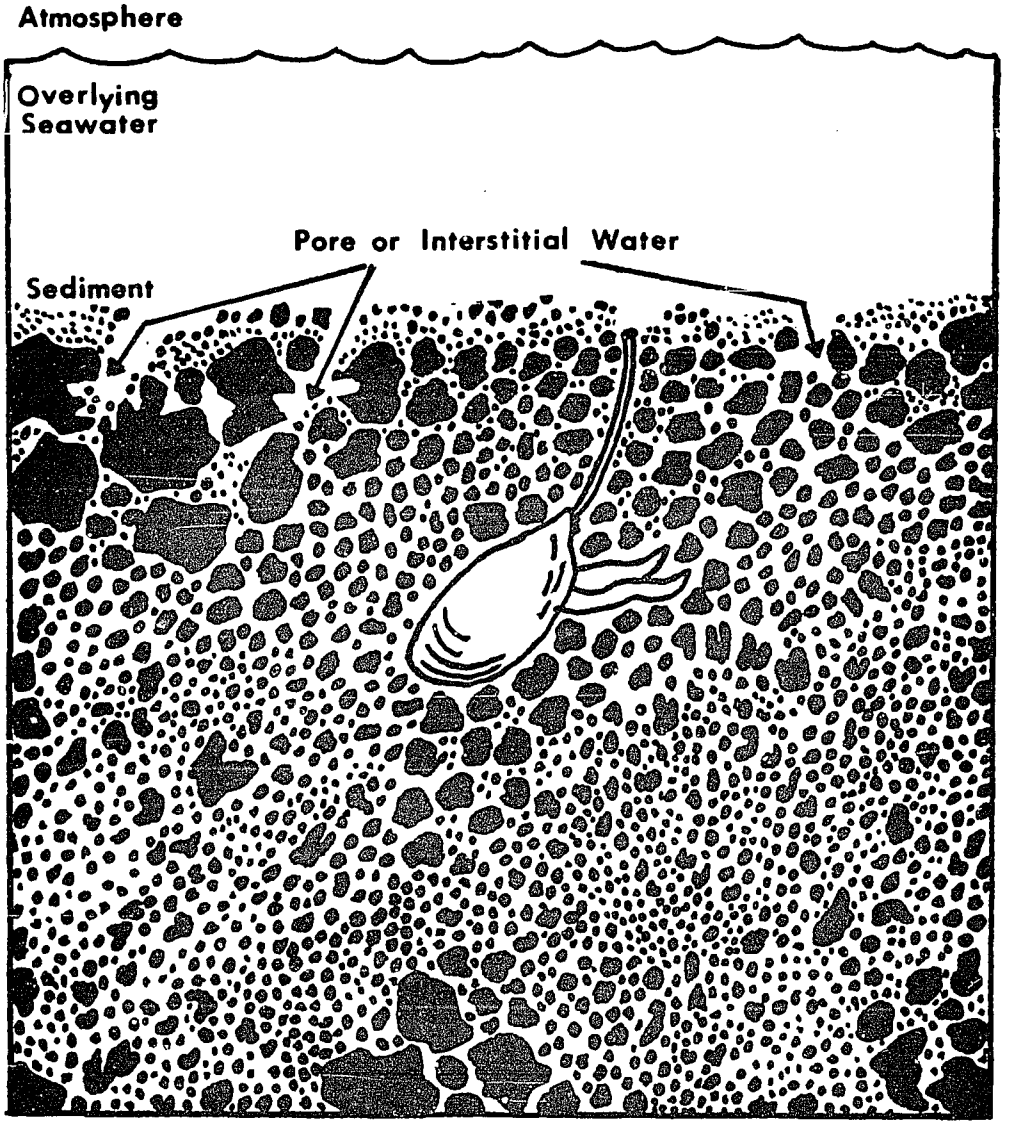

Figure 1-1. Schematic diagram showing the pore or interstitial water of marine sediments, which is represented by the white areas between the dark sediment grains.

with colloidal iron species, which occurs with the mixing of fresh and saline waters (Sieburth and Jensen, 1968; Matson, 1968; Gardner and Menzel, 1974; and Sholkovitz, 1976). In addition, Stephens and co-workers (1976), observed that roughly one half of the estuarine primary production during the year is deposited in the sediments.

The organic matter in the sea that is not deposited in sediments (99% of the total in the open ocean and, perhaps 50% in many estuaries), is rapidly recycled in the water column by the action of heterotrophic bacteria (Hobbie et al., 1968; Williams, 1970; Williams and Gray, 1970; and Andrews and Williams, 1971). Since these organisms preferably consume the most labile organic matter available, sediments are generally enriched in the more refractory material (Eglinton and Barnes, 1976). However, the details of this process are unclear and under intensive study at present (Gagosian and Stuermer, 1977). Of particular interest in this regard are recent organic geochemical studies of particles collected in sediment traps (Wiebe et al., 1976; Honjo, 1978; and Wakeham et al., 1980).

III. General Aspects of Early Diagenesis

On a weight basis, 90%+ of the material deposited in most marine sediments is inorganic, primarily sand and clay particles from land runoff in nearshore areas (Holland, 1978). Although purely inorganic reactions between the solid phases of sediments and pore waters have been observed (Sayles and Manheim, 1975; Gieskes et al., 1975; Perry et al., 1976; Manheim, 1976; and Sayles, 1979), it is the organic matter comprising the remaining 10% or less of deposited material that drives most of the chemical reactions occurring in marine sediments (Goldhaber and Kaplan, 1974). Many of these reactions involve struc-

tural changes in the detrital biomolecules originally deposited in the sediments. This process, especially in regard to the formation of geopolymers such as petroleum and coal, is of interest to organic geochemists. In addition, the remineralization of sedimentary organic matter is a process of critical importance to the maintenance of life in the sea and the global cycling of the elements C, N, P and S (Berner, 1977). However, the environmental modifications in the sediments accompanying the remineralization of sedimentary organic matter (particularly decreasing Eh and the production of reduced sulphur species), also induce many inorganic reactions. One example of this is the deposition of metal sulphide mineral phases in marine sediments (Berner, 1971; Turekian, 1977; and Lyons, 1979). All of these reactions, which are coupled to changes in the sedimentary organic matter, require the catalysis of bacteria in the sediments. The central role of bacteria in sedimentary geochemistry cannot be overemphasized.

Due to the action of aerobic bacteria in decomposing organic matter, sediments in the nearshore marine environment become anoxic at a relatively shallow depth (Berner, 1977). The depth at which anoxic conditions are established depends on a number of factors, including; the sedimentation rate (Goldhaber and Kaplan, 1975), the amounts and character of metabolizable organic matter (Berner, 1964 and 1970; and Lyons and Gaudette, 1979), and the relative activities of the aerobic bacteria (Hines, 1981). In most nearshore areas, with sedimentation rates in the range of 0.05 to 0.5 cm/year, the depth at which the concentration of O_2 in the pore water reaches zero varies seasonally from less than 1 cm (summer), to 4-10 cm (winter), (Rosenfeld, 1981; Klump and Martens, 1981; and Hines, 1981). This seasonal variation

is a function of temperature effects on bacterial activities. In the open ocean where sedimentation rates are considerably lower, the depth to complete O_2 exhaustion in the sediments may exceed 100 cm (Gieskes, 1975; and Manheim, 1976).

Below this oxic zone, the degradation of organic matter takes place as a result of bacterial anaerobic respiration. Anaerobic respiration involves the use of oxidants other than molecular O_2. Indeed, it is probable that aerobic respiration itself evolved from these more primitive modes of anaerobic respiration (Oparin, 1957; Woese, 1977; Degens, 1979; and Corliss et al., 1981). The metabolic pathways applicable to anaerobic respiration in marine sediments are presented in Table 1-1, along with their corresponding free energy changes. The simplest possible scenario for organic matter diagenesis in marine sediments is one in which sedimentary organic matter having the Redfield composition of $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$, (Redfield, 1958), is decomposed first by the metabolic pathway yielding the greatest free energy change per mole of organic carbon oxidized. When this oxidant is depleted, respiration will proceed by the next most efficient pathway, and so on until all oxidants are consumed or metabolizable organic matter is depleted. In sediments of the continental margin and open ocean where sedimentation rates are slow and the type of organic matter deposited is more refractory than that in nearshore areas, MnO_2, NO_3^- and Fe^{3+} reductions (processes 2, 3 and 4 in Table 1-1), are often important processes, extending to hundreds of meters into the sediments (Bender et al., 1977; and Froelich et al., 1979). However, in estuarine sediments with high organic matter contents, these metabolic pathways are of quantitatively minor importance due to the low concentrations of

Table 1-1. Sequence of oxidation reactions for sedimentary organic matter (adapted from Froelich et al., 1979).

Metabolic Pathway	ΔG^o (KJ/mole)
1. Aerobic Respiration	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \longrightarrow 106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$	-3190
2. MnO_2 Reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236\ MnO_2 + 472\ H^+ \longrightarrow 236\ Mn^2 + 106\ CO_2 + 8\ N_2 + H_3PO_4 + 366\ H_2O$	-3090[1] -3050[2] -2920[3]
3. Nitrate Reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4\ HNO_3 \longrightarrow 106\ CO_2 + 55.2\ N_2 + H_3PO_4 + 177.2\ H_2O$	-3030
4. Fe^{3+} Reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\ F_2O_3$ (or $424\ FeOOH$) $+ 848\ H^+ \longrightarrow 424\ Fe^{2+} + 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 530\ H_2O$ (or $742\ H_2O$)	-1410[4] -1330[5]
5. Sulphate Reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \longrightarrow 106\ CO_2 + 16\ NH_3 + 53\ S^{2-} + H_3PO_4 + 106\ H_2O$	-380
6. Carbonate Reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \longrightarrow 53\ CO_2 + 16\ NH_3 + H_3PO_4 + 53\ CH_4$	-350
7. Fermentation	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \longrightarrow 53\ C_2H_4O_2$ (acetic acid) $+ 16\ NH_3 + H_3PO_4$	-209

Table 1-1. continued.

1) ΔG^{o} for Birnessite ($MnO_{1.70}$ to MnO_2; contains hydroxyl)

2) ΔG^{o} for Nsutite ($MnO_{1.75}$ to MnO_2; contains hydroxyl)

3) ΔG^{o} for Pyrolusite (MnO_2)

4) ΔG^{o} for Hematite (Fe_2O_3)

5) ΔG^{o} for Limonitic Goethite (FeOOH)

these oxidants in seawater (Berner, 1971). Indeed, NO_3^- is often observed to be totally depleted in estuarine pore waters at depths of only a few millimeters to a few centimeters in the sediments (Vanderborght and Billen, 1975; Vanderborght et al., 1977; Sorensen, 1978; and Rosenfeld, 1981). The dominant respiratory pathway in most organic-rich, nearshore marine sediments is sulphate reduction (pathway 5 in Table 1-1), (Berner, 1972; Goldhaber and Kaplan, 1975; and Jorgensen, 1977). This metabolic process involves the use of sulphate as a terminal electron acceptor, and is favored in marine sediments due to the high concentration of sulphate in seawater (Berner, 1971). In many nearshore areas, the rates of sulphate reduction, particularly during the summer months, often exceed the supply of sulphate from the overlying seawater by molecular diffusion, and depletion of this ion in the pore water is observed (Berner, 1964 and 1970). The depth of complete sulphate depletion in the sediments may vary both spatially and seasonally, and depends on the relative bacterial activities and the metabolizability of the sedimentary organic matter. Carbonate reduction or methanogenesis (pathway 6 in Table 1-1), becomes important below the depth of complete sulphate depletion (Nissenbaum et al., 1972; Martens and Berner, 1974 and 1977; Barnes and Goldberg, 1976; and Winfrey and Zeikus, 1977). However, recent work has shown that sulphate reduction and methanogenesis may occur simultaneously, particularly in areas where large amounts of metabolizable sedimentary organic matter may reduce competition for substrates such as H_2 between these groups of bacteria (Oremland and Taylor, 1978). Methanogenic bacteria use HCO_3^- as a terminal electron acceptor for their metabolic pathway, producing CH_4 as a byproduct (Doelle, 1975). Both sulphate reducing and methano-

genic bacteria are obligate anaerobes, and exist only below the level of total O_2 depletion (Doelle, 1975).

A diverse group of heterotrophic bacteria, which carry out a variety of fermentative degradation of organic matter simultaneously with sulphate reduction and methanogenesis are found throughout the sediment column. (Winfrey et al., 1977; Oremland and Taylor, 1978; Barcelona, 1980; and Hines, 1981). Microbes have evolved a number of different fermentative pathways, however, all of these pathways utilize an organic compound as the terminal electron acceptor (Doelle, 1975). Microbial fermentation may produce a number of metabolic byproducts depending on the pathway, including: ethanol, acetic, formic, butyric, propionic and lactic acids and acetone (Doelle, 1975). A complex interrelationship exists among these various groups of anaerobic bacteria, and this will be discussed in some detail below. The net result of this combined heterotrophic bacterial activity is the stepwise degradation of complex organic biopolymers to inorganic species of C, N and P. A schematic representation of the sequence of metabolic pathways observed in nearshore marine sediments is presented in Figure 1-2.

Both sulphate reducing and methanogenic bacteria are incapable of metabolizing complex biomolecules such as polysaccharides, lignin and proteins (Doelle, 1975). As such, these bacteria are dependent on simple organic compounds produced by fermenters and other anaerobic heterogrophic bacteria as metabolic byproducts (Warford et al., 1979). One important group of compounds in this regard is the low molecular weight fatty acids (e.g. acetic acid, butyric acid, lactic acid and others). Recent determinations of these compounds in marine pore waters have revealed large concentrations, constituting up to 50% of the total dis-

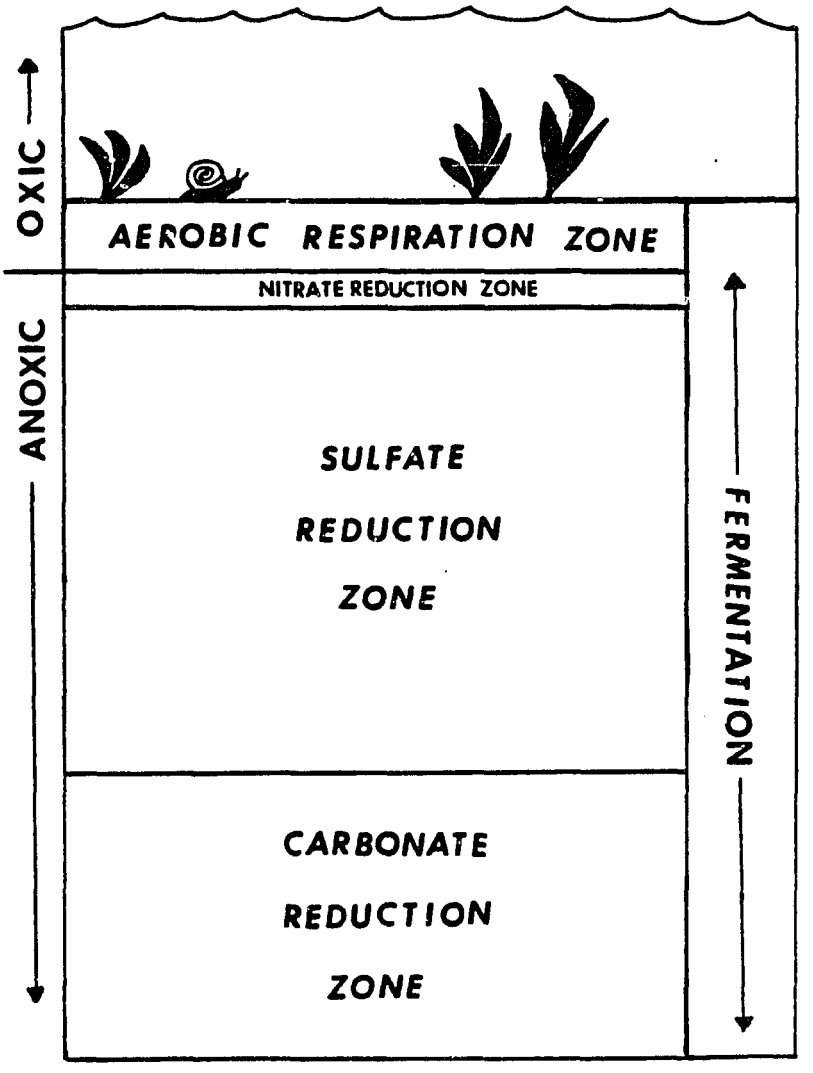

Figure 1-2. The sequence of metabolic reactions in nearshore marine sediments.

solved organic matter (Miller et al., 1979; and Barcelona, 1980). In these studies, formic acetic, n-butyric and iso-butyric acids were observed in particularly high amounts. Based on depth profiles of these volatile fatty acids, Barcelona (1980), has proposed a model of a sulphate reduction ecosystem. An adaptation of this model is illustrated in Figure 1-3. In this scenario, fermentive bacteria are primarily responsible for the degradation of refractory sedimentary organic matter, producing a number of monomeric substances as byproducts. These substances may then be passed on down the food chain through other anaerobic heterotrophic bacteria. Sulphate reducing and methanogenic bacteria represent the terminal organisms in this food chain. Sulphate reducing bacteria utilize 3 and 4 carbon fatty acids (e.g. lactic and succinic acids), produced by fermenters and other anaerobic heterotrophs, and release formic, acetic and butyric acids as byproducts of their metabolism. In addition, there is some evidence that sulphate reducing bacteria may utilize CH_4 produced by methanogens (Murry et al., 1978), as well as free amino acids (Smith and Klug, 1981). Methanogens are thought to utilize formic, acetic and butyric acids produced by fermenters and other anaerobic heterotrophs, and possibly fermenters, for their metabolism. Inorganic compounds such as CO_2, NH_3 and PO_4^{3-} are produced throughout this food chain as a consequence of the complete remineralization of sedimentary organic matter. However, mathematical modelling of anoxic sedimentary environments has illustrated the dominance of sulphate reduction (and probably methanogenesis), for the production of these inorganic ions; the final step in the remineralization of sedimentary organic matter (Berner, 1980). This model for a sulphate reduction ecosystem is also supported by the work of Peltzer (1979).

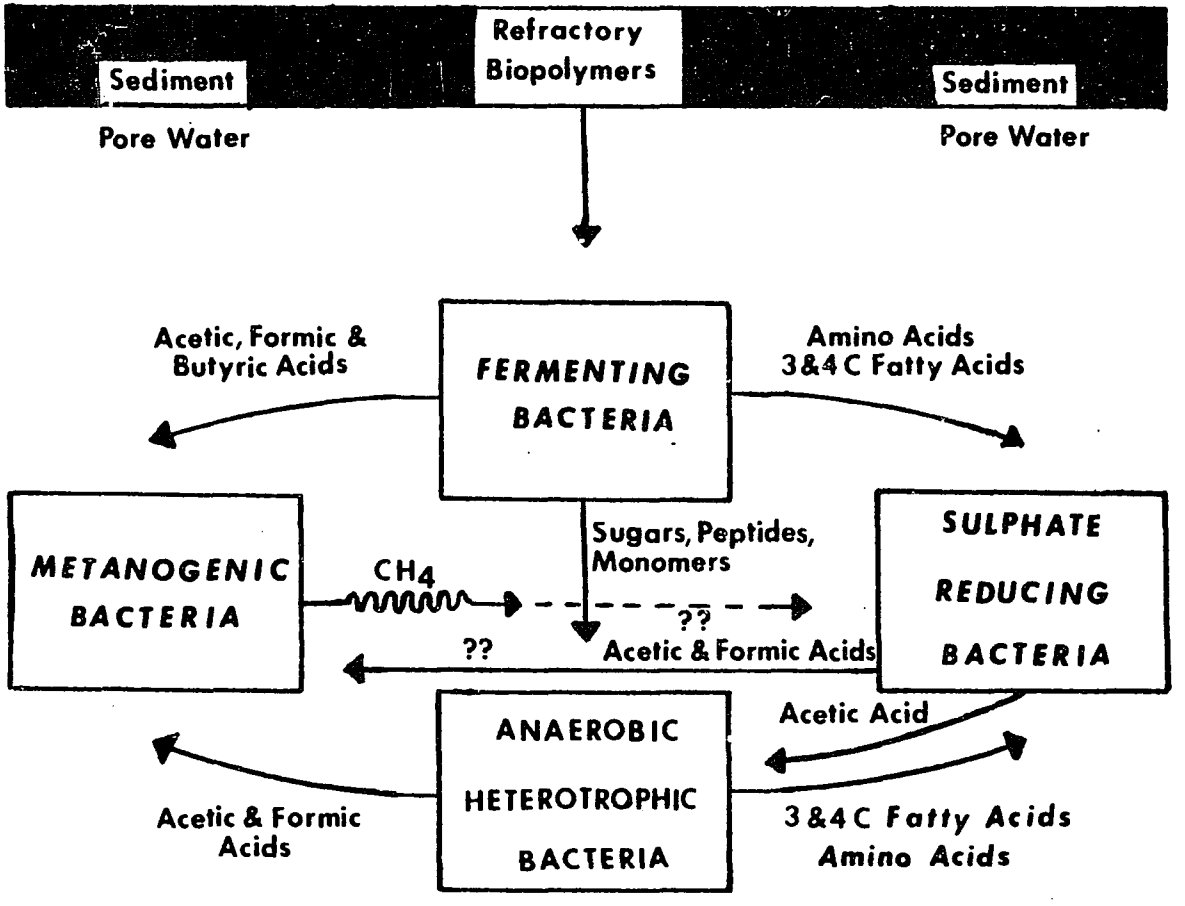

Figure 1-3. A schematic representation of a nearshore anoxic marine sediment ecosystem, adapted after Barcelona (1980).

However, these studies of this complex ecosystem may only be regarded as preliminary, and many of the details concerning the microbial breakdown of sedimentary organic matter must await further study.

As a result of the bacterial degradation of organic matter in marine sediments, the concentrations of a number of chemical species in the pore water are changed relative to their values in the overlying seawater. A number of these changes are summarized in Figure 1-4. As mentioned earlier, one of the first changes to take place is the depletion of dissolved O_2 in the pore water by the action of aerobic bacteria. In this oxic zone, nitrification also is generally observed, with increasing concentrations of NO_3^- in the pore water with depth (Vanderborght and Billen, 1975; Vanderborght et al., 1977; Grundmanis and Murray, 1977; and Lyons et al., 1980). Nitrification involves a two step process, in which ammonia produced from degraded organic nitrogen is first oxidized to NO_2^- by Nitrosomonas, and then to NO_3^- by Nitrobacter (Painter, 1970). Both of these species of bacteria are chemolithotrophic (e.g. autotrophs), and derive the energy necessary to synthesize organic matter from CO_2 from this oxidation process (Doelle, 1975). Below the level of complete O_2 depletion in the sediments, nitrate reduction becomes the next important metabolic process in the sediments, particularly in offshore areas. Bacterial nitrate reduction results in the removal of NO_3^- from the pore water, producing N_2 gas as its major nitrogen endproduct (see equation 3 in Table 1-1). In addition, there is some evidence to suggest that this process may serve as a source of N_2O to the ocean and atmosphere (Patrick and Reddy, 1976; Elkins et al., 1978; Sorensen, 1978; Kaplan et al., 1979; and Seitzinger et al., 1980). The effect of sequential nitrification and

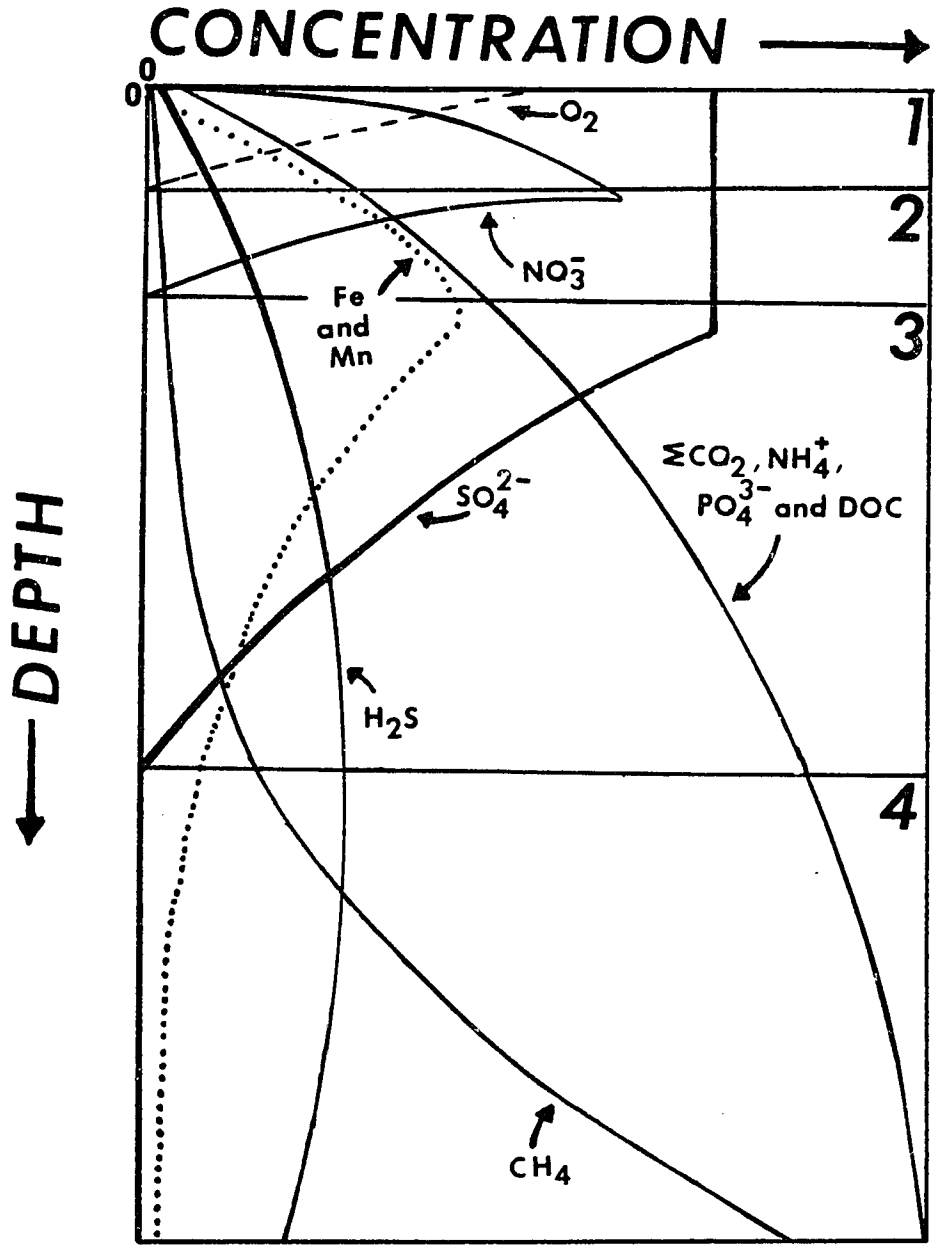

Figure 1-4. Idealized diagram of the changes observed in a number of chemical species in anoxic marine pore water as a consequence of the bacterial degradation of organic matter. Zone 1 corresponds to aerobic respiration, zone 2 to nitrate reduction, zone 3 to sulphate reduction and zone 4 to methanogenesis. See text for details.

nitrate reduction in marine sediments results in depth profiles for NO_3^- in the pore water similar to that illustrated in Figure 1-4. This type of trend has been successfully modeled using a two-layer approach by Vanderborght and his co-workers (1977). Following the complete removal of NO_3^- from the pore water by nitrate reduction, bacterial sulphate reduction results in the depletion of SO_4^{2-} in the pore water and the production of reduced sulphur species, particularly H_2S, as illustrated in Figure 1-4 (Berner, 1971). Based on equation 5 in Table 1-1, one mole of H_2S should be produced for every mole of SO_4^{2-} metabolized, with resulting mirror-image depth profiles for SO_4^{2-} and H_2S. However, the production of insoluble metal sulphides results in the removal of dissolved H_2S from pore water, and such mirror-image profiles are generally not observed (Goldhaber and Kaplan, 1974). Below the level of total SO_4^{2-} removal from the pore water, methanogenesis results in the production of CH_4 in the pore water (Claypool and Kaplan, 1974; Reeburgh and Heggie, 1974; Barnes and Goldberg, 1976; and Martens and Berner, 1977). The shape of the dissolved methane profile with depth, as illustrated in Figure 1-4, is established both by the diffusion of methane into the overlying seawater and consumption of CH_4 in the sulphate reduction zone. Throughout the sediment column, increases in the concentrations of inorganic carbon, ammonia and phosphate in the pore water with depth are generally observed, as illustrated in Figure 1-4 (Berner, 1971 and 1980). Values for the concentrations of these species in the pore water of nearshore sediments are often several hundred times those in the overlying seawater (Rittenberg et al., 1955; Nissenbaum et al., 1977; Sholkovitz, 1973; Bray, 1973; Berner, 1974; Suess, 1976; Murray et al., 1978; Martens and Goldhaber,

1978; Lyons et al., 1979b; and Rosenfeld, 1981). These ions are produced by the bacterial decomposition of sedimentary organic matter, as discussed earlier. In marine sediments, the terminal process in the sequence of bacterially mediated steps for the remineralization of organic C, N and P is, predominantly, sulphate reduction (Berner, 1971 and 1980). This process has been quantitatively modeled by Berner (1980).

As shown in Figure 1-4, dissolved organic carbon (DOC), in the pore water of marine sediments has been observed in concentrations many times that of the overlying seawater, and having depth profiles similar to that for inorganic carbon, ammonia and phosphate (Nissenbaum et al., 1972; Bella, 1972; Lindberg and Harriss, 1974; Krom and Sholkovitz, 1977; Lyons et al., 1978 and 1979c; and Barcelona, 1980). This DOC is undoubtably produced as a result of the incomplete oxidation of sedimentary organic matter by bacteria under anoxic conditions in the sediments. However, little is known concerning the nature and ultimate fate of this material, despite its potential involvement in the formation of geopolymers such as humic acid and petroleum (Berger, 1963; and Nissenbaum and Kaplan, 1972), and its role in the sulphate reduction ecosystem as outlined earlier.

The chemistry of metals in marine sediments is greatly influenced by the bacterial degradation of sedimentary organic matter. Of the various metal ions studied, the cycling of iron in marine sediments is perhaps best understood. However, a similar scenario may apply to other metals, especially manganese. The dominant form of iron in oxic surface waters is Fe(III), (Garrels and Christ, 1965). Various oxides and hydroxides of Fe(III), formed during weathering processes, are

transported to the ocean in rivers and streams primarily in the form of colloids and adsorbed coatings on detrital particles (Gibbs, 1973; Troup and Bricker, 1975; and Boyle et al., 1977). Upon mixing with higher ionic strength seawater, about 90% of the Fe(III) carried to the sea in river water is deposited in estuarine sediments by flocculation (Sholkovitz, 1976; Eckert and Sholkovitz, 1976; and Boyle et al., 1977). After burial in the sediments, the flocculated Fe(III) species become exposed to an environment deficient in oxygen as a result of bacterial degradation of sedimentary organic matter. Under these conditions, the precipitated and highly insoluble (at pH 7-8), Fe(III) species undergo rapid reduction to Fe(II), which is much more soluble under the pH conditions found in marine sediments. This process of reduction and dissolution of insoluble Fe(III) species in marine and freshwater sediments has been used to explain the higher iron concentrations of pore water compared to overlying water values (Rossman and Callendar, 1969; Callendar, 1969; Berner, 1971; Presley et al., 1972; Duchart et al., 1973 and Berner, 1980). Iron(II) can only exist in the absence of oxygen in such environments as anoxic marine sediments, since the oxidation of iron(II) to iron(III) is very rapid at pH 7-8 (Stumm and Lee, 1961). Competing with this dissolution of iron in anoxic marine sediments are a number of reactions which may remove iron(II) from the pore water by the formation of iron authigenic minerals. As a result of the decomposition of sedimentary organic matter by anaerobic bacteria (particularly sulphate reducing bacteria), the concentrations of sulphide, bicarbonate and phosphate are enriched in pore water, several orders of magnitude over their overlying seawater values. If the concentrations of these species and dissolved iron(II), are sufficiently

high, the precipitation of a number of authigenic minerals may result, including: mackinawite (FeS), greigite (Fe_3S_4), pyrite (FeS_2), siderite ($FeCO_3$), and vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$), (Berner, 1971). Previous workers, using thermodynamic calculations of the saturation state of various mineral phases have suggested that siderite, vivianite and mackinawite may control the iron concentrations of pore water (Berner, 1967; and Troup, 1974). In addition, recent studies have suggested that the complexation of iron(II), by dissolved organic matter may also be important in controlling the concentration of this metal in marine pore waters (Nissenbaum and Swaine, 1976; Krom and Sholkovitz, 1977; Lyons et al., 1979a; Templeton, 1980; and Lammela, 1981). This sequence of reactions for iron in marine sediments (e.g. dissolution of iron by the reduction of Fe(III), to Fe(II), followed by precipitation of authigenic iron mineral phases), results in depth profiles for dissolved iron in pore waters similar to that illustrated in Figure 1-4.

IV. Organic Matter in the Pore Water of Marine Sediments

Organic substances dissolved in marine pore water may come from two sources: 1) those organic compounds buried with the overlying seawater and 2) organic compounds produced as byproducts of the bacterial degradation of sedimentary organic matter. Since the dissolved organic carbon content of pore water is commonly 10 to 100 times that in the overlying seawater, the second source discussed above is by far the more important (Krom and Sholkovitz, 1977). Thus, studies of organic compounds in pore water may provide useful insights into the diagenetic processes occurring in marine sediments. Despite this, surprisingly

few studies of organic matter in marine pore waters have been conducted, although there have been a number of investigations on the accumulation of inorganic species in pore water (Berner et al., 1970; Sholkovitz, 1973; Holdren et al., 1975; Grundmanis and Murray, 1976; Lyons and Fitzgerald, 1976; Goldhaber et al., 1977; Martens and Goldhaber, 1978; and Rosenfeld, 1981).

Dissolved organic matter in marine pore waters may play an important role in a number of diagenetic reactions. The condensation of amino acids and sugars (e.g. the Maillard reaction), has been proposed as a mechanism for the production of humic substances in marine sediments (Berger, 1963; Nissenbaum and Kaplan, 1972; and Welte, 1973). The series of reactions that may be involved in this process is illustrated in Figure 1-5. However, these reactions alone cannot account for the long-chain, aliphatic components of sedimentary humic substances (Nissenbaum and Kaplan, 1972; Hatcher et al., 1980; Hatcher, 1980). Thus, bonding of lipids to amino sugar condensates through ester or amide linkages or at sites of unsaturation may be involved in the humification process. Recent work has confirmed that amino sugar condensates can react with and bind lipids under laboratory conditions (Larter and Douglas, 1980). Pore water may play a key role in this process by providing a fluid medium in which these reactions may occur and in the maintenance of anoxic conditions. Indeed, Nissenbaum and co-workers (1972), showed the presence of polymeric organic matter in anoxic marine pore waters with characteristics similar to those of fulvic and humic acids. In addition to this, dissolved organic matter in marine pore water may be extremely important in the transfer of energy between different microorganisms in anoxic sediments. Low molecular

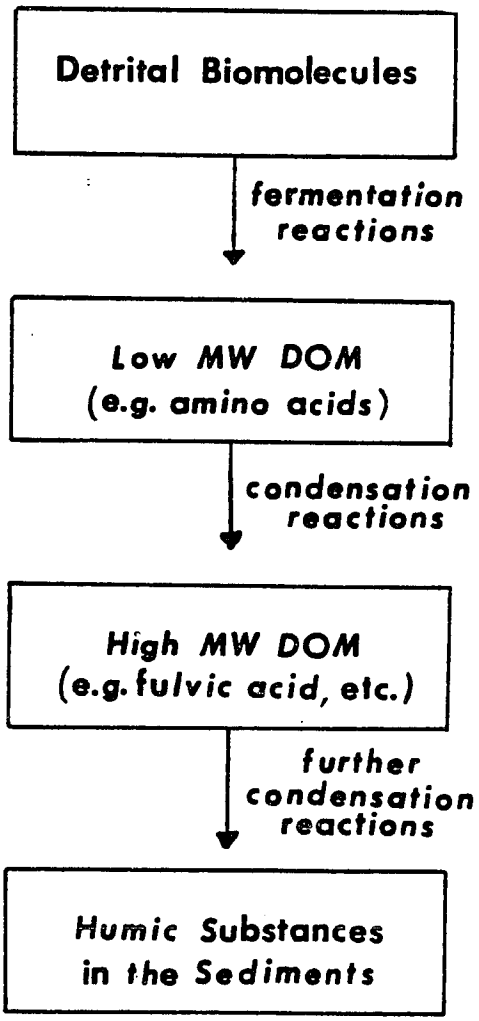

Figure 1-5. Proposed mechanism for the formation of humic substances in marine sediments. Adapted from Krom and Sholkovitz (1977). DOM = dissolved organic matter.

weight fatty acids appear to be particularly important in this respect (Miller et al., 1979; Peltzer, 1979; and Barcelona, 1980). Finally, dissolved organic matter in pore water probably plays an important role in the sedimentary geochemistry of a number of inorganic chemical species. For example, Berner et al., (1970, 1978 and 1979), have suggested that dissolved organic matter inhibits the precipitation of $CaCO_3$ in supersaturated pore waters by inactivating nucleation sites. In addition, organic compounds in pore water have been shown to be important in the transport and speciation of trace metals in anoxic sediments (Nissenbaum and Swaine, 1976; Lyons et al., 1979a; Templeton, 1980; Lammela, 1981; and Boulegue et al., 1982). Complexation of trace metals by organic matter in marine pore waters may explain why concentrations of dissolved metals in anoxic sediments often exceed those expected based on equilibrium with various mineral phases (Presley et al., 1972; Holdren et al., 1975; and Lyons and Fitzgerald, 1976).

As in other areas of organic geochemistry, studies of organic matter in marine pore waters have taken two approaches: 1) the analysis of the characteristics of the bulk or total organic matter and 2) the determination of specific organic compounds in the pore water. Both of these approaches have advantages and disadvantages. The bulk approach has the advantage of focusing on the chemical composition of the total or large fractions of the total organic matter dissolved in marine pore waters. The major difficulty with this approach is that it reflects the sum of a number of simultaneously occurring transformations, involving a large number of different organic compounds with varying functionalities, stabilities and reactivities (Gagosian and Stvermer,

1977). This makes the problem of separating out the different types of diagenetic transformations taking place very difficult. The specific compounds approach, on the other hand, allows the study of one specific transformation at a time. However, this approach has the disadvantage of concentrating on only a tiny fraction of the total organic matter present in the pore water of marine sediments. This makes interpretation of the overall diagenetic processes in marine sediments difficult. Obviously, future work in organic geochemistry should emphasize a combination of both the bulk organic matter and specific compounds approach. This would maximize the advantages of each, while minimizing their respective disadvantages.

The bulk properties of pore water organic matter studied to date include: dissolved organic carbon analysis (Krom and Sholkovitz, 1977), ultraviolet/visible absorption (Nissenbaum et al., 1977; and Krom and Sholkovitz, 1977), infrared absorption (Nissenbaum et al., 1972; and Krom and Sholkovitz, 1977), fluorescense (Ewald, 1979), and molecular size determination (Lindberg and Harriss, 1974; and Krom and Sholkovitz, 1977). Specific compounds that have been determined include amino acids (Henrichs and Farrington, 1979; and Gardner and Hanson, 1979) carbohydrates (Nissenbaum et al., 1972; and Lyons et al., 1979), fatty acids (Miller et al., 1979; and Barcelona, 1980), and n-alkanes (Nissenbaum et al., 1972). The details of these various studies on the organic geochemistry of marine pore waters are discussed in later chapters of this dissertation in relation to specific aspects of this study.

V. Purpose of this Study

The objective of this research was to enhance our understanding

of the complex nature of the bio-organic and organic-organic reactions occurring during early diagenesis. A complete understanding of these processes in anoxic marine sediments is desirable for two reasons: 1) the life processes of anaerobic bacteria result in the production of a number of byproducts (e.g. reduced sulphur species and inorganic carbon), which affect diagenetic reactions, most notably those influencing the mobility of trace metals in the environment and 2) changes in the character of organic matter resulting from anaerobic decomposition and organic-organic reactions may be important in the later formation of geopolymers such as humic substances, kerogen, coal and petroleum. As mentioned earlier, studies of these processes should emphasize the analysis of pore water organic matter rather than organic material in the solid sediments, since variations in pore water composition are much more sensitive indicators of chemical and biological reactions occurring in this environment. Since very little has been accomplished in this area of research, the principal aim of the work presented in this dissertation was a comprehensive study of some of the more fundamental aspects of the organic geochemistry of estuarine pore water. In this context, three major goals were set forth:

1) To determine what sampling and sample handling precautions must be taken to maintain the integrity of the dissolved organic matter in anoxic pore water samples, particularly in regard to problems of oxidation.

2) To conduct a comprehensive survey of dissolved organic carbon (DOC), distributions in estuarine pore water, including studies of the lateral, depth and seasonal variation of DOC and its molecular size distribution.

3) To investigate some of the bulk characteristics of pore water organic matter, particularly emphasizing the development of a separation method for this material using high pressure liquid

chromatography.

In addition to these major goals, studies of some specific organic compounds in pore water and of inorganic species intimately involved in the diagenetic transformations of organic matter in anoxic marine sediments were planned. One aspect of this research that was emphasized was the relationship between organic geochemistry and microbiology in anoxic marine sediments, and the results reported in this dissertation will often be discussed in relation to microbiological studies conducted concurrently (Hines, 1981).

VI. Outline of Dissertation

The basic format of this dissertation is one of separate chapters, each relating to a different aspect of the research conducted and more or less self-contained. The present chapter has been a brief introduction to the organic geochemistry of anoxic marine sediments, and outlined the overall goals of the dissertation research. Chapter 2, the experimental section, discusses in detail the sampling area (i.e. The Great Bay Estuary, New Hampshire), as well as all aspects of the sampling, sample handling and analytical procedures used. Chapters 3, 4, 5 and 6 present the results of the research and discuss in detail what these results may indicate regarding the diagenetic reactions occurring in anoxic marine sediments. Chapters 3, 5 and 6 correspond, respectively to the major goals 1, 2 and 3 discussed earlier, while Chapter 4 is an overview of the descriptive chemistry of Great Bay anoxic sediments. Each of these chapters contains an introduction which discusses the perinent literature in these areas. In addition, a conclusion section is included in these chapters to summarize the major points of interest. Many of the numerical results for Chapters

4 and 5 are presented in Appendices so as not to clutter these chapters with a large number of tables. Finally, Chapter 7 is a summary of the overall conclusions and significance of the dissertation work and also presents some suggestions for future studies.

CHAPTER 2

EXPERIMENTAL

I. Study Area

Samples of anoxic marine sediment for this study were obtained from the Great Bay Estuarine System, New Hampshire. The location of this estuary with respect to the Gulf of Maine region is illustrated in Figure 2-1. The Great Bay system consists of two major embayments (Great Bay and Little Bay), and seven major tidal rivers (see Figure 2-2), comprising an area of approximately 43 km^2 (Armstrong et al., 1976). A large percentage of this area is composed of shallow tidal mudflats, with about 45% of the bay exposed at low tide (Jackson, 1944). The average depth of Great Bay at low tide is only about 2 m, although tidal channels may reach depths of up to 22 m (Armstrong et al., 1976). Sedimentation rates in the estuary have recently been estimated to be in the range of 0.1 - 0.2 cm/yr (Leavitt, 1980). Sediment size determinations for the Great Bay system have shown the overall sediment type to be a sandy silt, although considerable variation may occur from site to site (Armstrong et al., 1976; and Leavitt, 1980). Salinities within the estuary vary seasonally, and during this study were observed to range from only a few parts per thousand (^{o}/oo or ppt), to 30 ^{o}/oo.

A total of five sites within the Great Bay system were sampled for this work (Figure 2-2). The five sites were chosen based on a number of criteria, including: organic matter content of the sediments, geography of the site, ease of sampling and the extent of previous work

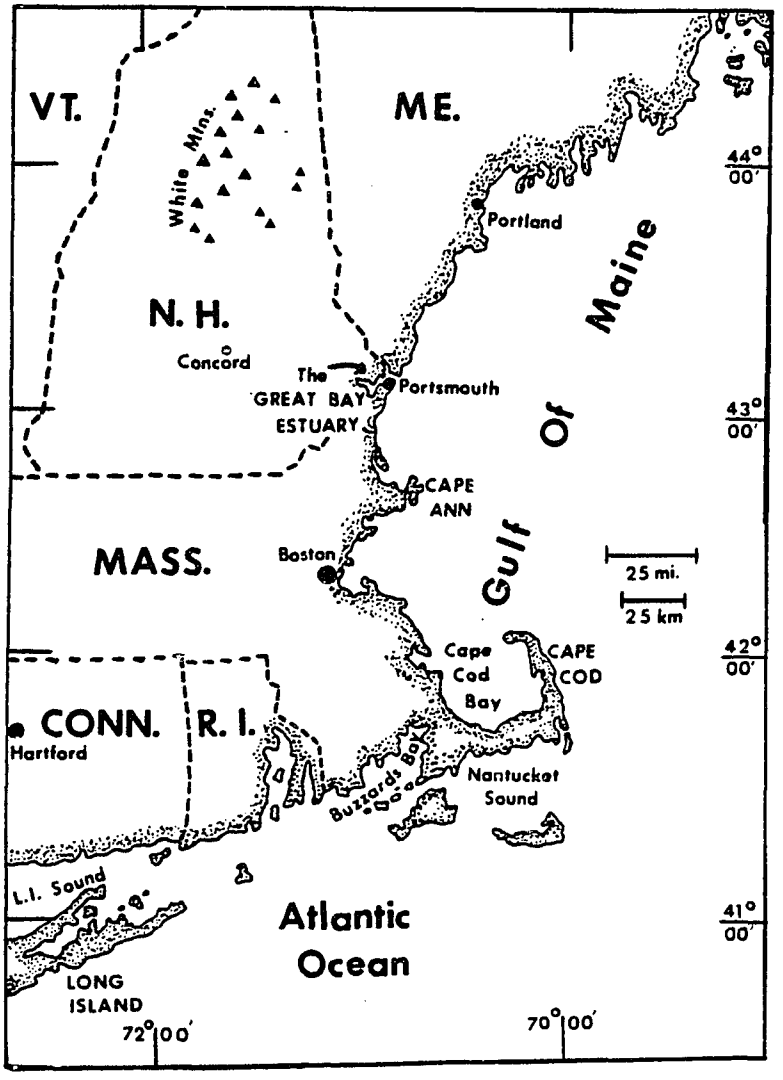

Figure 2-1. The location of the Great Bay Estuary, New Hampshire with respect to the Gulf of Maine region.

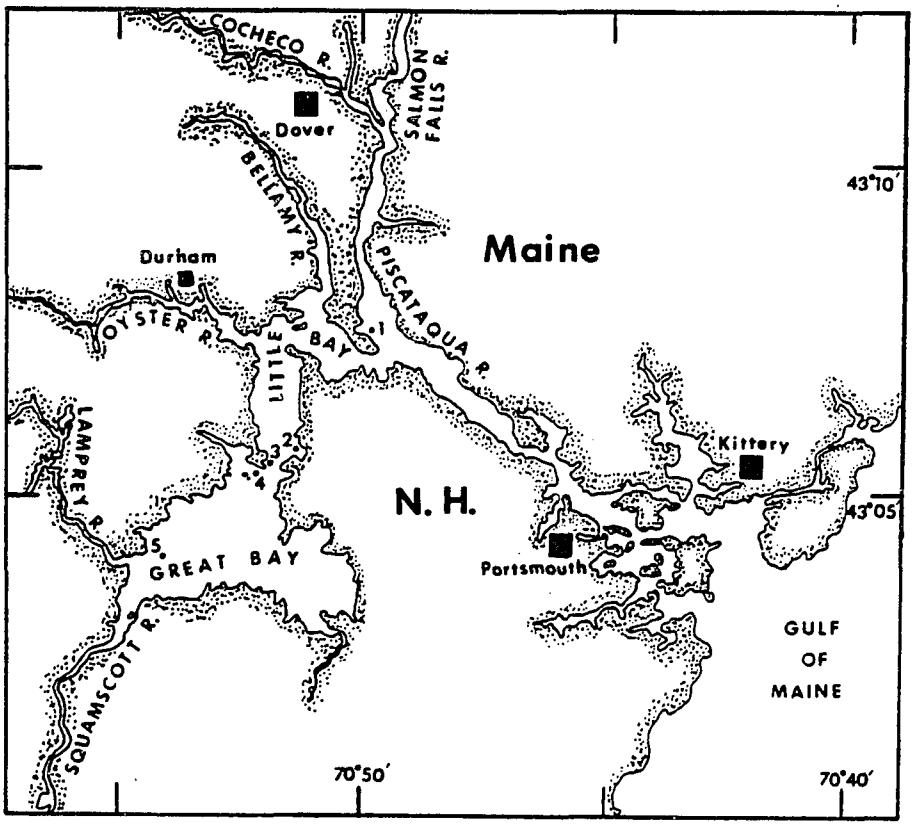

Figure 2-2. The Great Bay Estuary, New Hampshire showing the location of the five sampling locations: Site 1 (Piscataqua River); Site 2 (Welsh Cove; Site 3 (Adams Cove); Site 4 (Footman Islands); and Site 5 (Squamscott River).

at the location. Site 1, chosen for its location at the northern extreme of the estuary in the Piscataqua River, is in a region of high tidal current flow. In addition to its location, previous work on the organic geochemistry of the sediments at this site (Lyons and Gaudette, 1979), made it suitable for further work. Sites 2, 3 and 4 are all located in the central portion of the bay system. Site 2, located on the eastern side of the bay in Welsh Cove, has a higher sand content (and, thus, a lower organic content), in the surface sediments, compared to sites along the western shore of the estuary. In general, sites along the eastern shore of Great Bay exhibit a higher sand content in the surficial sediments than western sites, possibly a result of sediment sorting by wind fetch from the predominantly westerly winds, and/or due to lower riverine inflow to the eastern side (Anderson, personal communication). Site 2, then, is representative of the eastern shore of the bay system. Site 3 is located in Adams Cove, directly across Little Bay from site 2 and adjacent to the University of New Hampshire's Jackson Estuarine Laboratory. Due to its proximity to laboratory facilities, this site has been extensively sampled, and a great deal of geochemical baseline data has been generated (e.g. Armstrong et al., 1979; Lyons et al., 1979b; Wilson and Lyons, 1980; and Hines, 1981). Site 4, located near the Footman Islands in Great Bay proper, is in an eelgrass (Zostera marina), bed. This site and site 5, which is situated in the extreme southwest corner of Great Bay near the mouths of the Squamscott and Lamprey Rivers, were found to have the highest percentages of organic matter in the sediments of the five areas sampled. In addition, these two sites have been previously studied with regard to their sedimentary geochemistry (Armstrong et al., 1979; Lyons

et al., 1979b; Lyons and Gaudette, 1979; Orem and Gaudette, 1979; Leavitt, 1980; and Hines, 1981).

II. Sample Collection

Sediment samples for this work were obtained using two types of coring devices: box cores and gravity cores. Box cores were used to study processes occurring in the top 15 cm of sediment during the earliest stages of organic diagenesis when bacterial activities are highest. Gravity cores, on the other hand, were useful for investigating organic matter alteration taking place during later stages of diagenesis, and involving both bacterial and purely chemical reactions.

Box cores were obtained utilizing a hand operated lexane box corer (25 x 10 x 30 cm). Cores were taken below the low tide line in approximately 0.5 m of water by manually pushing the box corer into the sediment. Overlying water, obtained along with the sediment in the coring device, was left in the box corer to help maintain the sediment at ambient temperatures, until return to the laboratory for processing. Following sampling, the box corer with the sediment sample was placed in a plastic cooler filled with seawater from the site, and immediately returned to the laboratory for processing. In no case did the elapsed time between sample collection and processing exceed 30 minutes.

Gravity cores were obtained from on board the R. V. Jere Chase, utilizing a stainless steel coring device with 8 cm (i.d.), polycarbonate core liners. Upon retrieval, the overlying water was quickly decanted off, and the core liner immediately capped and placed in a nitrogen filled plastic core carrier. Cores were returned to the laboratory for processing as soon after sampling as practicable, usually within one hour. Cores up to 150 cm deep were obtained using this

technique.

Samples of overlying water were collected during a number of sampling dates for comparison of the concentrations of various chemical species with sediment pore water concentrations. On sampling dates involving box coring, overlying water samples were collected by hand in glass (for organic species), and plastic (for inorganic species), bottles. For gravity coring, samples of overlying water were collected with a Niskin bottle from the R. V. Jere Chase. After collection the water samples were transferred from the Niskin sampler to glass and plastic sampling bottles. Overlying water samples from both box and gravity core sampling dates were stored in the dark in a styrofoam cooler until return to the laboratory for processing.

Prior to a sampling date, cleaning of both the box corer and the gravity core liners was accomplished by soaking overnight in dilute hydrochloric acid (10% v/v), followed by extensive washing with distilled/deionized (D/D), water. Accessory equipment also coming in contact with the sediment sample (e.g. caps for the core liners, and the silicone stoppers for the box corer), as well as the Niskin sampler were cleaned in a similar manner. Glass bottles for sampling the overlying water were cleaned by soaking overnight in concentrated nitric acid, rinsing thoroughly with D/D water and baking in a muffle furnace at 450^{o}C for a minimum of two hours. Plastic bottles were soaked overnight in concentrated hydrochloric acid and rinsed thoroughly with D/D water. In addition, both glass and plastic sampling bottles were rinsed at least twice with the overlying water sample prior to collecting a sample for chemical analysis. Plastic gloves were normally worn during all phases of sample collection to minimize organic contamination.

For studies of the seasonal variation of chemical species in sediment pore water, it is important to establish a single sampling point within a locale in order to eliminate as much as possible any confusion lateral inhomogeneities in the sediment may contribute to the observed seasonal trend. In this study, box coring sites were established with a marker placed into the sediments, and cores taken over the course of the year were generally within 2 m of one another. Care was also taken to avoid sampling disturbed areas (e.g. footprints, and previous box core depressions). For gravity coring, the problem of establishing a single sampling point was more difficult. Normally, a permanent reference point (e.g. a marker buoy or a large tree on shore), was used and gravity cores taken with regard to the reference. Cores taken at a site over the course of a year were generally within 15 m of one another.

III. Sample Processing

Immediately after returning a sediment core to the laboratory, processing of the core was begun. The overall sample processing scheme for both box and gravity cores is illustrated in Figure 2-3. Gravity cores were immediately extruded onto aluminum foil in a glove bag, which had been pre-purged with nitrogen gas. For box cores, the water overlying the sediment in the coring device was quickly removed by siphoning, and the entire box core placed in a pre-purged, nitrogen filled glove bag. The sediment was then extruded from the box corer onto aluminum foil in the glove bag for sectioning. In general, box cores were cut into 2 cm sections as a function of depth; while gravity core sections were either 5, 10 or 15 cm thick.

An important point concerning the processing of anoxic marine

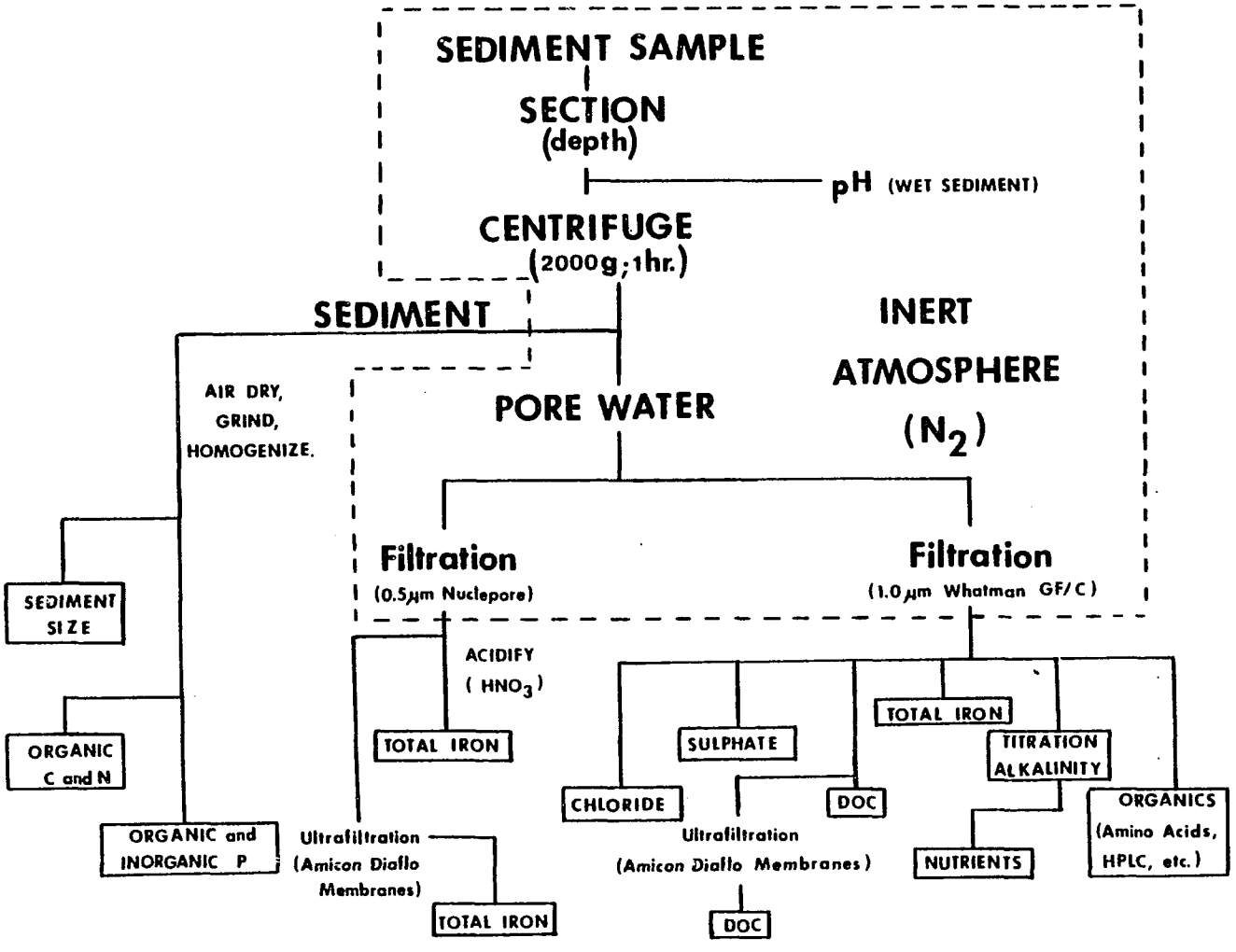

Figure 2-3. General sample processing scheme.

sediments is the necessity of maintaining oxygen free conditions. Earlier workers have shown that exposure of these sediments to atmospheric oxygen can result in serious losses of a number of inorganic chemical species from the pore water (Bray et al., 1973; Troup et al., 1974; Loder et al., 1978; and Lyons et al., 1979d), and changes in the nature of the sedimentary organic matter (Templeton, 1980). Therefore, in this study oxygen free conditions were stringently maintained during all sample processing and handling.

Following sectioning of the sample, separation of the pore water from the sediment was accomplished by centrifugation. Individual core sections were homogenized and scooped into precleaned, 250 ml, linear polyethylene centrifuge bottles inside the glove bag. The samples were then centrifuged at 2,000 g for one hour at exactly in situ surface sediment temperatures, under a nitrogen atmosphere. A Damon/IEC (Needham Hts., Mass.), model B20A refrigerated centrifuge was used for this procedure. A portion of the homogenized sediment from each core section prior to centrifugation was placed in a small, pre-cleaned plastic vial for pH analysis (Figure 2-3). These capped vials were stored in the glove bag under nitrogen until the pH of the samples could be measured.

The centrifuge bottles, containing the separated pore water and sediment after centrifugation, were immediately returned to the nitrogen filled glove bag for filtration. As illustrated in Figure 2-3, two separate filtrations were performed on the pore water. All samples for organic matter analysis were filtered through 1 μm (nominal pore size), glass fibre filters (Whatman, GF/C), in an all glass filtering apparatus (Millipore Corporation; Bedford, Mass). Glass filters and all glass

filtering devices have been recommended for the analysis of organic matter in seawater (Gordon, 1969; and Sharp, 1972 and 1975), since effective cleaning to remove contaminating organic compounds (normally by baking at 450°C), is possible. Pore water for the analysis of chloride and sulphate ions, titration alkalinity and nutrients (nitrate plus nitrite, ammonia, phosphate and silicate), was also filtered using this system. However, sample reserved for the analysis of dissolved iron was filtered through 0.5 µm (nominal pore size), Nuclepore membrane filters and all plastic or teflon filtering devices (Chau and Lum-Shue-Chan, 1974; Ramamoorthy and Kushner, 1975; Batley and Florence, 1976; Jackson, 1978; and Lyons et al., 1979a and 1980), since glass is known to adsorb metal ions (Robertson 1968; Struempler, 1973; Isaaq and Zielinski, 1974; Gardiner, 1974; and King et al., 1974).

The filtered pore water was transferred into various bottles (glass for organic matter analysis and plastic for all others) using a Gilson automatic pipette (Rainin Corporation; Brighton, Mass.), with precleaned (see discussion of cleaning procedures below), plastic tips and stored for future chemical analysis. Samples for qualitative organic analysis (e.g. ultrafiltration, HPLC, and spectroscopic analysis), were stored under nitrogen in sealed (serum stoppers), glass bottles in a glove bag. Sodium azide (10 µl of 0.1 $\underline{M}$ NaN_3 per 1 ml of pore water), was added to these samples to retard bacterial decomposition (Hines, personal communication). Pore water for the analysis of specific organic compounds (e.g. amino acids, carbohydrates, etc.), was stored frozen (-25°C), in capped glass bottles. Aliquots for DOC analysis were fixed with concentrated phosphoric acid (0.2 ml H_3PO_4 per 1 ml pore water), and also stored frozen. Phosphoric acid was added for a

number of reasons: 1) to enhance the evolution of inorganic carbon from the sample prior to DOC analysis, 2) to help prevent precipitation of organic matter during the freezing process and 3) to help retard bacterial action by maintaining a low pH in the sample. Pore water for sulfate analysis was spiked with zinc acetate (0.2 ml of 0.1 M $(CH_3COO^-)_2 Zn \cdot 2H_2O$ per 1 ml sample), to precipitate sulphide. Howarth (1978), observed that soluble sulphides in pore water may be oxidized to sulphate during analysis and storage, thus leading to erroneously high sulphate concentrations unless removed by precipitation as a zinc sulphide. The colloidal zinc sulphide was removed from the supernatant pore water by centrifugation, and the sulphide free sample stored under refrigeration (5^oC), in capped plastic bottles. Pore water for chloride analysis was also stored refrigerated in capped plastic bottles to minimize any problems with evaporation. Aliquots for titration alkalinity were stored under nitrogen in capped plastic bottles and refrigerated until analysis, usually within eight hours of sample collection. Following titration, these samples (now acidified to pH <4), were stored frozen in capped plastic bottles for future nutrient analyses. Pore water samples for total iron were spiked with ultrapure HNO_3 (1 µl per ml of sample), to enhance release of iron complexed to organic matter and to prevent 'wall effects' during storage. Iron samples were stored in tightly capped plastic bottles at room temperature.

Sediment samples, following removal of the pore water, were extruded from the centrifuge bottles and placed on squares of aluminum foil (covered to avoid contamination), for air drying. When dried, the sediment was ground with a mortar and pestle and stored in plastic bags in a desiccator for future analyses.

Prior to any sampling date, careful attention was paid to the precleaning of all glass and plasticware to be used during the sample processing procedure and for sample storage. Small sized glassware was soaked overnight in concentrated nitric acid, rinsed thoroughly with D/D water and, finally, baked in a muffle furnace at 450°C. Oversized glassware was cleaned in an analagous manner, except that baking was impossible due to the size of the pieces. Glass fibre filters were soaked overnight in D/D water and baked at 450°C to remove contaminating organics. All plasticware (e.g. storage bottles, centrifuge bottles, pipette tips, filtering equipment, etc.), was cleaned by soaking for a minimum of 48 hours in concentrated hydrochloric acid followed by extensive rinsing with D/D water. Nuclepore membrane filters were cleaned in a similar manner. The only variation from these cleaning procedures was for cores to be analyzed for trace organic compounds (e.g. amino acids, carbohydrates, etc.). For these cores, final rinsing of all glass and plasticware was performed using D/D water that had been UV irradiated for a minimum of 4 hours to further destroy any contaminating organic matter. In addition to these cleaning procedures, care was taken during all sample handling to avoid touching the sample with anything but precleaned equipment. However, even with such careful cleaning and handling procedures contamination may occur, and appropriate blanks were always run to determine the extent of contamination.

IV. Analytical Methods

A. Sediment Analyses

Air dried and ground sediment samples were analyzed for organic carbon, nitrogen and phosphorus and inorganic phosphorus content. In addition, the proportions of sand, silt and clay in the sediment were

determined. Organic carbon and nitrogen was measured using a Perkin Elmer model 240 B Elemental Analyzer (Perkin Elmer Corporation, Norwalk, Connecticut). Cystine and cyclohexanone-2, 4-dinitrophenylhydrozone were used as standards. The extraction procedure of Aspil Murphy and Riley (1962); modified by Bray (1973), was used to determine organic and inorganic phosphorus. Sediment size was determined using standard wet sieving and pipette techniques (Folk, 1974).

B. Inorganic Species in Pore Water

A number of inorganic species in pore water were routinely determined during this study, including: chloride, sulphate, nitrate plus nitrite, ammonia, phosphate, silicate and total iron. In addition, pH and titration alkalinity were also measured on a routine basis.

The pH of the pore water was obtained by direct insertion of a combination pH electrode (Corning model 476115, Corning Science Products, Horseheads, New York), into the wet sediment. Previous workers have observed that pH measurements of extruded pore water are often anomalously high, probably as a result of loss of CO_2 during sample processing (Siever, 1961; Troup, 1974; and Lyons, 1979). This problem is discussed in more detail in Chapter 3. An Orion Microprocessor Ionalyzer 901 pH meter was used for this procedure (Orion Research, Cambridge, Mass.). Calibration of the pH meter with pH 7 and 10 standard buffers (VWR Scientific, Boston, Mass.), was performed before and after each sample measurement. One disadvantage of this method for the determination of the pH of marine sediments was the long equilibration time required to obtain a stable reading; usually 10-15 minutes for each sample. In addition, care must be taken to avoid blockage of the glass frit on the electrode by sediment grains and organic detritus.

Titration alkalinities of pore water samples from this study were determined by a method similar to that used by Gieskes and Rogers (1973). Approximately 0.1 M HCl was prepared for this titration by dilution of reagent grade HCl with D/D water. The ionic strength of this solution was adjusted, approximately, to that of the pore water with reagent grade sodium chloride, to prevent the formation of high junction potentials. The exact concentration of the HCl solution was determined by titration versus an NaOH solution (phenolpthalein indicator), which had been standardized with potassium hydrogen phthalate. A 2.0 ml capacity micrometer buret (Roger Gilmont Instruments, Inc., Great Neck, New York), was used for this analysis. Changes in pH values during the titration of the pore water samples with the HCl solution were measured with an Orion semimicro combination pH electrode and Microprocessor Ionalyzer model 901 pH meter. The pH's of the pore water samples were reduced to values between 3 and 4, and the volumes of HCl required were recorded. Titration alkalinities were calculated using the method of Grasshoff, (1976).

Chloride ion concentrations were determined using a micro titration method, requiring only 1 ml of sample. This method utilizes silver nitrate (about 0.2 M), as the titrant and sodium fluoresceinate as the indicator (Kalle, 1951; Fajans, 1956; and Grasshoff, 1976). Sulphate concentrations were measured using two different techniques: 1) a gravimetric method after Presley (1971), and 2) a titration method developed by Howarth (1978). Copenhagen standard seawater of known chlorinity was utilized as a standard for both the chloride and sulphate analyses. Preparation of standard curves showed the chloride titration and both sulphate methods to be linear over the range of sample concen-

trations encountered in this study. All chemicals used in these analyses were of reagent grade, and D/D water was used in making up all solutions. In addition, all glassware was scrupulously cleaned, as recommended by Grasshoff (1976), for the chloride titration and Presley (1971), and Howarth (1978), for the sulphate methods.

Nitrate plus nitrite, ammonia, phosphate and silicate concentrations in pore water samples were determined using a Technicon Auto Analyzer II system (Technicon Corporation, Tarrytown, New York), and standard technicon methods, as modified for seawater by Glibert and Loder (1977). Nutrient analyses were performed on pore water samples previously used for titration alkalinity determinations in order to conserve sample, as mentioned earlier. Due to the high concentrations of ammonia, phosphate and silicate found in pore water, dilution of the samples with D/D water prior to analysis for these ions was necessary. For samples from box cores, dilutions of 30:1 were usually sufficient. However, for longer cores the correct dilutions were often difficult to predict, and the reanalysis of some samples was necessary. Dilutions of up to 1000:1 in the deeper sections of some gravity cores were needed. Because of the high dilutions needed for the analysis of ammonia, phosphate and silicate in these samples, no refractive index or salinity corrections were needed (Loder and Glibert, 1976). Problems of carryover were avoided by running each sample in triplicate and by discarding any peaks obviously affected by carryover. The autoanalyzer system used in this study was equipped with a two channel recorder which allowed the determination of two chemical species at a time. Usually, ammonia and phosphate were determined together, and nitrate plus nitrite and silicate individually. Appropriate standards and blanks, as

recommended by Glibert and Loder (1977), were run with each batch of samples. All chemicals used were of reagent grade quality, and D/D water was used in preparing all solutions. Prior to analysis, samples were removed from the freezer and allowed to thaw at room temperature overnight (about 10 hours). Any samples exhibiting a precipitate were further acidified with dilute HCl and allowed to sit an additional period of time in an attempt to dissolve the precipitate. If this procedure failed, the sample was discarded.

A serious problem was encountered in the analysis of nitrate plus nitrite in pore water from Great Bay sediments. As discussed earlier (see Chapter 1), thermodynamics predicts that bacterial denitrification processes should remove all nitrate from the pore water of anoxic marine sediments prior to the onset of sulphate reduction. In the real world, of course, the line of demarcation between the zones of bacterial denitrification and sulphate reduction is not sharp. However, nitrate concentrations are still expected to show decreasing concentrations with depth; and to approach a concentration of zero very rapidly in organic rich, nearshore sediments. Indeed, previous workers have observed this type of profile for nitrate in anoxic marine sediments (Vanderborght and Billen, 1975; Wilson, 1978; Sorensen, 1978; Koike and Hattori, 1979; Suess et al., 1980; and Rosenfeld, 1981). Following the procedures outlined above for the handling and storage of pore water samples for nutrient analyses, unrealistically high nitrate concentrations (up to 500 μM), were observed, even at depths of 100 cm. Blanks of D/D water run through the entire sample processing procedure indicated the problem was not one of contamination. In the presence of oxygen, ammonia may be oxydized to nitrate. However, the inorganic re-

action:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O,$$

although favored thermodynamically ($\Delta G^o = -64.12$ kcal/mole), (Garrels and Christ, 1965), is very slow at room temperature (Berner, 1971). This reaction may be catalyzed by the action of aerobic bacteria; the process being termed nitrification (Graety et al., 1973; Vanderborght and Billen, 1975; Rajendran and Venugopalan, 1976; Patrick and Reddy, 1976; and Suess et al., 1980). However, the fact that these samples were stored acidified and frozen mitigates nitrification having produced these anamolous nitrate plus nitrite values. For this same reason, the oxidation of organic nitrogen compounds to nitrate by bacterial action seems unlikely. In later cores, pore water samples for nitrate plus nitrite analysis were stored unacidified under anoxic conditions. These results are presented in Table 2-1. Although nitrate plus nitrite values from these cores are much more realistic, the irregular depth profiles and the failure of nitrate plus nitrite concentrations to approach zero at depth is worrisome. It is possible that some oxidation of ammonia to nitrate may have occurred during analysis. Thus, the accuracy of these results remains questionable. It seems likely that some inorganic oxidation process was the cause of the unrealistically high nitrate plus nitrite concentrations. However, the nature of this reaction is uncertain, and further work is needed on this problem.

Total dissolved iron in pore water was determined using the spectrophotometric method of Murray and Gill (1978). These samples were stored for at least one week (spiked with concentrated, ultrapure HNO_3), prior to analysis to allow complete dissolution of any complexed or colloidal iron.

Table 2-1. Nitrate plus nitrite concentrations in cores stored unacidified and anoxically.

Core PS-I
Site 2 (Welsh Cove)
Date: 6-10-78

Depth (cm)	$NO_3^- + NO_2^-$ (μM)
0-5	3.1
5-10	6.9
10-15	5.8
15-20	3.7
20-25	9.1
25-30	7.9
30-35	7.9
35-40	6.9
40-45	9.3
45-55	9.9
55-65	10.2

Core PS-II
Site 4 (Footman Islands)
Date: 6-30-78

Depth (cm)	$NO_3^- + NO_2^-$ (μM)
0-5	1.4
5-10	3.0
10-20	13.2
20-30	0.7
30-40	3.6
40-50	2.0
50-60	1.7
60-70	1.1
70-80	0.6
80-85	2.4

Core PS-III
Site 1 (Piscataqua River)
Date: 7-19-78

Depth (cm)	$NO_3^- + NO_2^-$ (μM)
0-5	4.8
5-10	5.0
10-20	7.2
20-30	6.1

Core PS-IV
Site 4 (Squamscott River)
Date: 8-10-78

Depth (cm)	$NO_3^- + NO_2^-$ (μM)
0-10	2.2
10-20	6.5
20-30	-
30-40	3.6
40-50	3.9
50-60	6.8
60-70	7.4
70-80	3.1
80-90	2.4
90-100	4.5

Table 2-1. continued.

Core FI-B
Site 4 (Footman Islands)
Date: 6-10-79

Depth (cm)	$NO_3^- + NO_2^-$ (μM)
0-2	0.7
2-4	0.2
4-6	0.9
6-8	0.9
8-10	0.9
10-12	0.9

C. Dissolved Organic Carbon

The determination of dissolved organic carbon (DOC), in pore water and overlying seawater in this study was accomplished using a Sybron-Barnstead PHOTOchem organic carbon analyzer (Barnstead Company, Boston, Massachusetts). This instrument uses an ultraviolet photochemical oxidation system for the destruction of organic matter, and detects the CO_2 produced by this oxidation with a conductivity cell. This detector measures the change in the specific resistance of ultrapure water in the conductivity cell by the dissolution of the CO_2 produced by the oxidation process. A pre-oxidative measurement of the inorganic carbon in a sample is also performed by the instrument for correction of the conductance measured at the end of the oxidative cycle. A complete description of the theory and instrumentation of this method was presented by Poirer and Wood (1978).

The DOC content of pore water was routinely measured by injection of 1.0 ml of sample or standard and 1.0 ml of 0.148 M H_3PO_4 into the instrument. Primary standard grade potassium hydrogen phthalate (KHP), dissolved in an artificial seawater solution of approximately the same salinity as the samples was used as a calibration standard. Standard concentrations of 30 mgC/l and 100 mgC/l were used in the analysis of pore water from box cores and gravity cores, respectively. The phosphoric acid solution was injected along with the sample to enhance the evolution of CO_2 from the pore water. Poirer and Wood (1978), have reported that the addition of 5% (W/V), potassium peroxidisulphate ($K_2S_2O_8$), to the H_3PO_4 solution greatly increases the efficiency of the ultraviolet digestion. This effect is illustrated in Figure 2-4 for a solution of 100 mgC/l KHP in D/D water injected both with and without

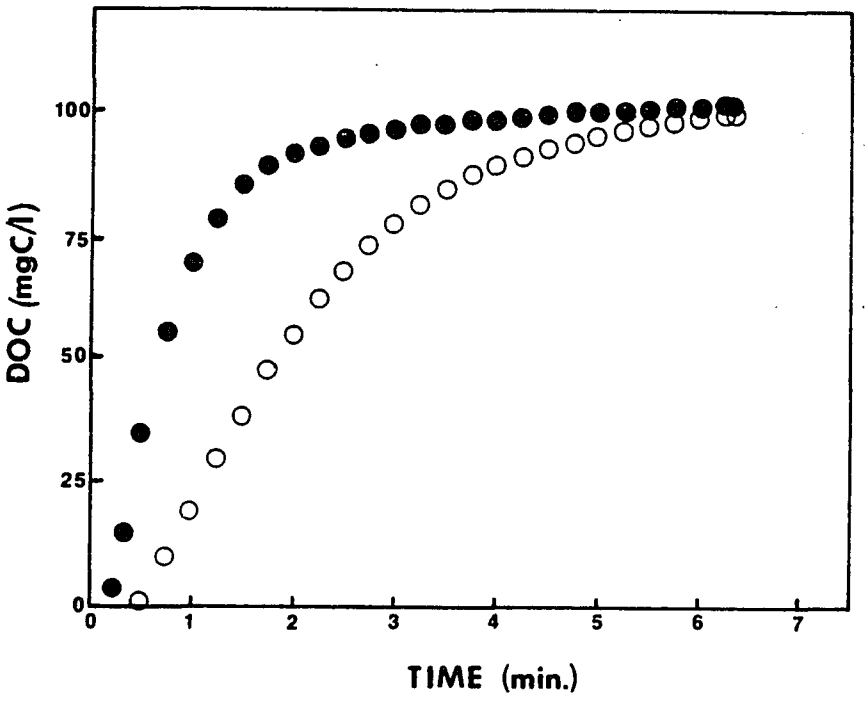

Figure 2-4. The kinetics of photochemical oxidation on a 100 mgC/l potassium hydrogen phthalate solution injected with 0.148 M H_3PO_4 plus 5% $K_2S_2O_8$ (•), and injected with 0.148 M H_3PO_4 only (o).

$K_2S_2O_8$. In both curves, essentially 100% recovery of the KHP solution was achieved. However, the kinetics of the oxidation process were considerably faster in the sample injected with the $K_2S_2O_8$.

A series of experiments were carried out to evaluate possible matrix interferences (i.e. salt effects), with this DOC method, prior to its routine use with pore water. The initial results of this work were somewhat disheartening, as a severe reduction in the recovery of both 100 mgC/l and 50 mgC/l KHP standards dissolved in artificial seawater was observed, even at a salinity of only 1 °/oo. This effect was discovered to involve an interaction between the $K_2S_2O_8$ added to the H_3PO_4 solution and NaCl. This is clearly demonstrated from the data presented in Table 2-2. For 100 mgC/l and 50 mgC/l KHP standards injected with 0.148 M H_3PO_4 only, a small salt effect was observed at salinities above 50 °/oo. Recoveries of at least 94% were observed for these standards even at salinities as high as 150 °/oo. In contrast, these same standards injected with 0.148 M H_3PO_4 containing $K_2S_2O_8$ showed only about 60% recovery at a salinity of just 1 °/oo. This recovery was observed to decrease with increasing salinity to a relatively constant value of about 40% at salinities of 3 °/oo to 25 °/oo. Curiously, at salinities above 25 °/oo, this trend reversed with the recovery reaching 60% at a salinity of 150 °/oo. The exact nature of the interaction between NaCl and $K_2S_2O_8$ is uncertain, but appears to involve a reduction in the kinetics of oxidation, as illustrated by the plots in Figure 2-5. It is known that at low pH the presence of $K_2S_2O_8$ in a solution of NaCl will cause oxidation of chloride to chlorine (Collins and Williams, 1977). The production of chlorine gas in the instrument may result in attenuation of the ultraviolet light and/or interfere with the detection sys-

Table 2-2. Salt effects in DOC analysis with Barnstead PHOTOchem Organic Carbon Analyzer.

Acid: 0.148 M H_3PO_4

Salinity (°/oo)	100 mgC/l Standard	50 mgC/l Standard	0 mgC/l Blank
0	101.0	50.5	- 0.5
5	101.7	50.8	- 0.6
10	101.2	50.7	- 0.6
25	100.8	50.4	- 0.9
50	99.9	50.0	- 1.3
100	96.6	48.8	- 1.6
150	91.6	46.7	- 2.1

Acid: 0.148 M H_3PO_4 with 5°/oo (W/V) $K_2S_2O_8$

Salinity (°/oo)	100 mgC/l Standard	50 mgC/l Standard	0 mgC/l Blank
0	101.1	50.1	- 1.1
1	63.1	29.6	0.4
3	40.6	25.4	0.7
5	38.3	23.7	0.6
10	40.3	24.0	0.8
25	36.8	22.7	0.8
50	44.1	25.9	0.9
100	51.8	31.8	4.7
150	66.6	37.5	6.8

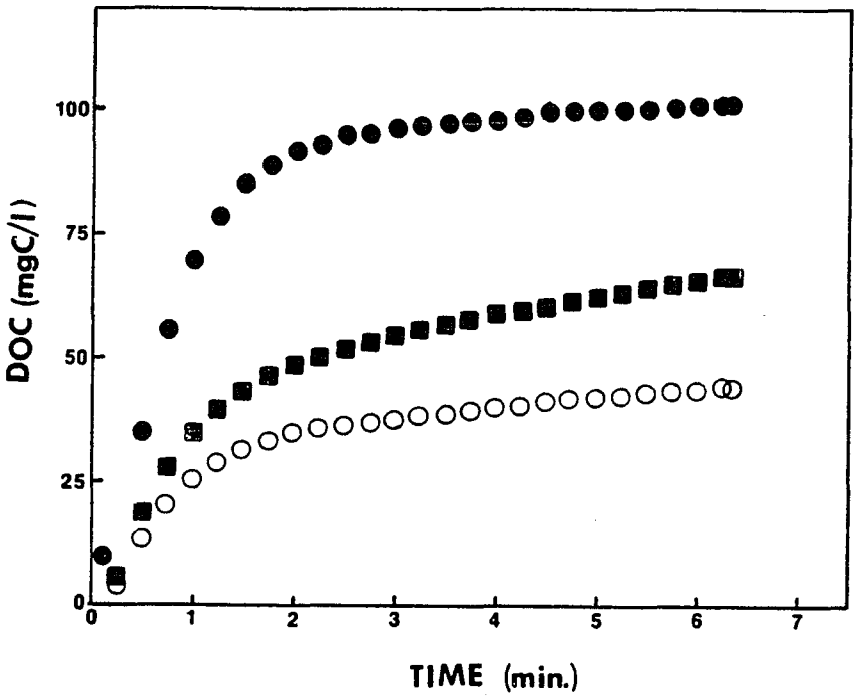

Figure 2-5. Kinetics of oxidation of a 100 mgC/l potassium hydrogen phthalate standard injected with a 0.148 M H_3PO_4 plus 5% (W/V), $K_2S_2O_8$ solution, at various chlorinities of the standard: 0°/oo (●), 50 °/oo (o), and 150 °/oo (■). The standards were made by dissolving phthalate and various amounts of sodium chloride in D/D water.

tem. A similar salt effect was observed in a Technicon DOC auto-analyzer system, which also uses ultraviolet digestion with $K_2S_2O_8$ addition, although with a different detector system. In conclusion, caution should be exercised in the use of ultraviolet digestion systems with $K_2S_2O_8$ for the analysis of saltwater samples.

Standard curves for DOC were prepared by injecting different volumes of 5 and 10 mgC/l KHP solutions with 0.148 M H_3PO_4 into the organic carbon analyzer. These plots were linear only for standards dissolved in D/D water. KHP standards dissolved in artificial seawater with salinities of 10 °/oo and 25 °/oo produced standard curves of the form: $y = \ln x$. The injection of different volumes of pore water and overlying seawater samples with 0.148 M H_3PO_4 into the instrument also resulted in non-linear curves of this form. These results are illustrated in Figure 2-6. This non-linear behavior of organic carbon standards and samples dissolved in saltwater, again, may be a consequence of the oxidation of chloride to chlorine during the ultraviolet digestion. The presence of $K_2S_2O_8$ in the 0.148 M H_3PO_4 apparently only exacerbates this oxidation of chloride to chlorine. As a consequence of this non-linear behavior, care was taken in this study to assure that standards were made up in artificial seawater of about the same salinity as the samples to be analyzed. This was not a serious difficulty since the chlorinities of the pore water samples from Great Bay were observed to vary only slightly from site to site and seasonally (see Chapter 4). However, this non-linearity may be a problem if samples having widely ranging salinity values are to be measured. It is also recommended that consistent volumes of both samples and standards be injected, to avoid having to make corrections based on a non-

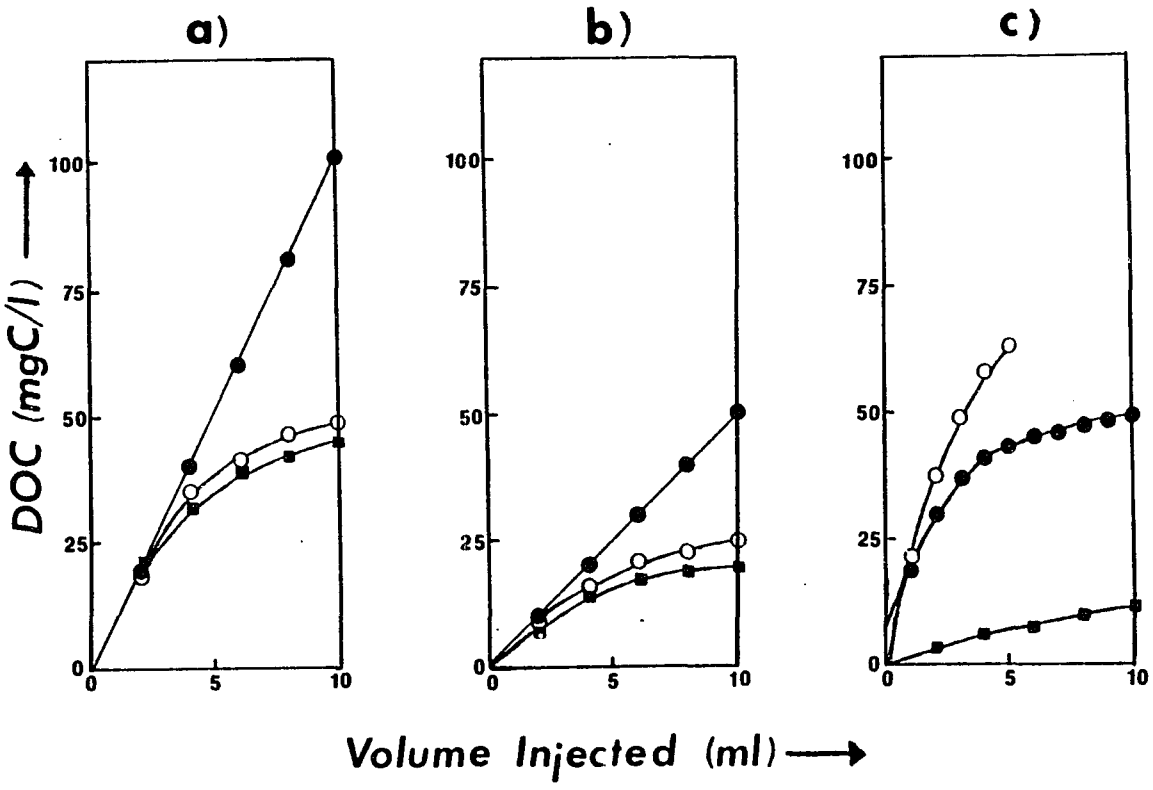

Figure 2-6. Standard curves for DOC analysis: a) 10 mgC/l KHP standard; b) 5 mgC/l KHP standard; and c) pore water (● and o), and seawater (■) samples. The KHP standards in a) and b) were made up in D/D water of 0 °/oo (●), 10 °/oo (o), and 25 °/oo (■), salinity. Note the non-linear standard curves for saltwater samples and standards.

linear standard curve. This was generally not a problem in this study, since the pore water samples from Great Bay had sufficiently high DOC concentrations to allow consistent 1.0 ml injections.

One advantage of this method of DOC analysis compared to other methods used (Gershey et al., 1979), is that a preliminary sparging step to remove dissolved inorganic carbon is not needed. This sparging step may remove volatile organic compounds from the sample prior to analysis, resulting in an underestimate of the DOC (Mackinnon, 1979). This may be a serious problem in anoxic marine pore waters where volatile fatty acids may constitute a significant fraction of the DOC (Barcelona, 1980). However, work by Poirer and Wood (1978), with the PHOTOchem organic carbon analyzer has shown essentially 100% recoveries in DOC analyses of solutions of acetic acid and other volatile organic compounds.

One persistent criticism of ultraviolet photochemical oxidation methods of DOC analysis has been that these techniques fail to oxidize all of the organic carbon present in a sample (Afghan et al., 1970). However, recent work has shown ultraviolet photochemical oxidation to be as effective as high temperature combustion for the analysis of DOC in seawater (Gershey et al., 1979). In order to evaluate the effectiveness of ultraviolet photochemical oxidation for the analysis of anoxic marine pore water, a sample of pore water from Great Bay sediments was desalted and freeze dried; and the carbon content of the sample determined by high temperature combustion in a Perkin Elmer model 240 B Elemental Analyzer. A weighed portion of this freeze dried sample was then redissolved in a known volume of D/D water and the DOC content of this solution determined by ultraviolet photochemical oxidation in the PHOTO-

chem organic carbon analyzer. The average organic carbon content of this sample as determined by photochemical oxidation (triplicate analyses), was 7.6% lower than that obtained by high temperature combustion (triplicate analyses). However, this was within the measurement error of the elemental analyzer. Thus, the ultraviolet photochemical oxidation method appears to be nearly 100% efficient in the analysis of DOC in anoxic pore water. Truitt (personal communication), has also observed the PHOTOchem organic carbon analyzer to be approximately 100% efficient in oxidizing organic carbon in soil fulvic acid; and Templeton (1980), found good agreement between photochemical and high temperature comustion analysis of organic carbon inorganic matter extracted from anoxic marine sediments.

D. Specific Organic Compounds

The analysis of three groups of specific organic compounds in pore water from Great Bay sediments was attempted in this study: amino acids, carbohydrates and low molecular weight fatty acids. The determination of these biochemically active compounds was emphasized in order to trace some of the biogeochemical processes affecting organic matter in marine sediments.

Amino acids were primarily determined using a fluorescence technique adapted for pore water after Udenfriend et al. (1972). Since most amino acids are not naturally fluorescent this method employs a reagent (fluorescamine), which reacts with primary amino groups to form a fluorescent product. This reaction is complete in 1000 msec, and fluorescence detection is achieved at an excitation wavelength of 395 nm and an emission wavelength of 480 nm (Udenfriend et al., 1972).

The procedure used in this study involved reaction of 2 ml of

pore water with 0.2 ml of a borate buffer (12.4 g H_3BO_4/l D/D water, titrated to pH 9 with 3 M NaOH), followed by reaction of this mixture with 0.6 ml of a fluorescamine solution (25 mg fluorescamine dissolved in 100 ml distilled acetone). The boric acid used was of analytical grade and was recrystallized from D/D water. Reagent grade acetone was triple distilled in an all glass still prior to use. Fluorescamine was obtained from Pierce Chemical Company (Rockford, Illinois). All reagents were stored in pre-cleaned glass bottles to avoid contamination. The reaction was carried out in 5 ml glass test tubes, and fluorescence measurements were made using a Perkin-Elmer 204 Fluorescence Spectrophotometer (Perkin-Elmer Corporation, Norwalk, Connecticut). A blank must be run for each sample to correct for background fluorescence in the pore water. Suitable corrections for contamination and background fluorescence in the buffer and fluorescamine solution must also be made. A solution of 24 common amino acids, each at a concentration of 0.01 µgN/250 ml 0.1 M HCl was used as a primary standard. A few milligrams of $HgCl_2$ was added to this solution to retard bacterial degradation. Appropriate dilutions of this primary standard were made for use as working standards. A linear response was observed over the range of amino acid concentrations observed in the pore water (Figure 2-7). In addition to free amino acids, dissolved total amino acids (e.g. peptides, proteins and free amino acids), may be determined using this fluorescence method. However, this requires a preliminary hydrolysis step (6 M HCl under a N_2 atmosphere at 110°C for 22 hours), to break up proteins and peptides prior to analysis (Moore and Stein, 1963).

The fluorescamine method allows for the determination of gross amino acid concentrations, but gives no information regarding individual

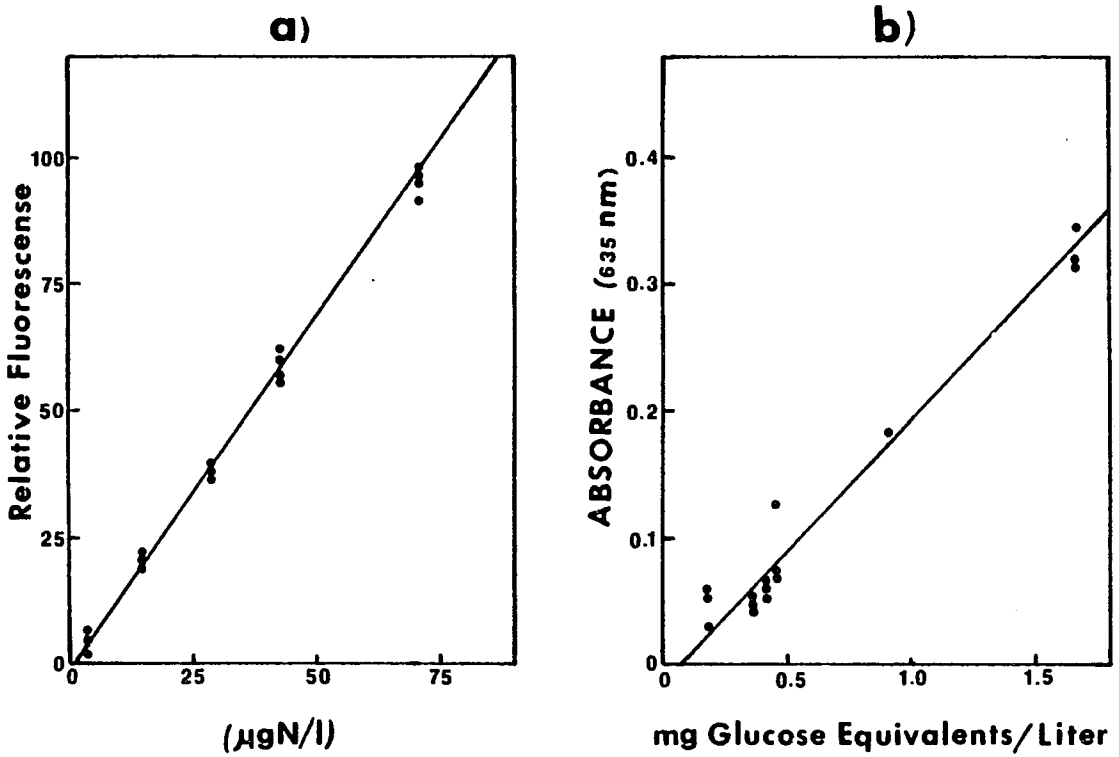

Figure 2-7. Standard plots for the amino acid fluorescence method (a), and the spectrophotometric method for carbohydrates (b).

amino acid concentrations. In addition, it is not strictly specific for amino acids and may react with other primary amines in pore water. However, this technique offers a number of advantages over methods of individual amino acid analysis in instances when it is not essential to know individual amino acid concentrations, including: 1) simplicity of analysis, 2) speed of analysis, 3) low cost per sample, 4) no ammonia interference and 5) little sample volume required. The last two advantages are particularly important in pore water work. In order to assess the accuracy of the fluorescence method, the free amino acid concentration of a pore water sample was determined using both the fluorescamine technique and a method using an amino acid analyzer (Henrich and Farrington, 1979; and Gardner and Hanson, 1979). A Beckman 118 CL amino acid analyzer (Beckman Instruments Inc., Fullerton, California), coupled to a Varian CDS 118C integrator/recorder (Varian Associates, Palo Alto, California), was used for this study. Individual amino acid concentrations obtained in this manner were summed for comparison to values obtained using the fluorescence technique. The results of this study indicated that the fluorescence method overestimates the free amino acid content of pore water only by about 5%. Thus, this method may be employed with confidence for the analysis of the amino acid content of pore water. Indeed, amino acid concentrations in pore water from Great Bay sediments obtained in this manner were quite similar to those reported by other workers in nearshore sedimentary environments (Starikova and Korzhikova, 1972; Clark et al., 1972; Henrichs and Farrington, 1979; and Gardner and Hanson, 1979).

Carbohydrates in pore water were determined by the spectrophotometric methods of Johnson and Sieburth (1977), and Burney and

Sieburth (1977). In the initial application of this method to pore water, an interference resulting in the development of a brown/black instead of the expected amber color was encountered. It was suspected that this interference was caused by dissolved H_2S in the pore water samples. Acidification and purging of the pore water samples with N_2 gas prior to analysis was successful in removing the interference. Glucose was used as a standard for this study, and all carbohydrate values are reported in terms of glucose equivalent weights. Standard curves were linear over the range of carbohydrate concentrations observed in the pore water (see Figure 2-7).

One of the original goals of this study was the determination of low molecular weight fatty acids (e.g. acetic acid, butyric acid, pyruvic acid, etc.), in pore water from Great Bay anoxic sediments. As discussed earlier (see Chapter 1), these compounds are extremely important in bacterial metabolism. Despite this, few studies of the concentrations and distribution of these compounds in marine sediments and pore water have been reported. Originally, the method of Miller et al. (1979), was used for this study. This procedure involves the extraction of the organic acids from the pore water into ultrapure ethyl acetate at a temperature of 50°C and a pH of 1.5 for two hours. The extracted acids are then separated and quantified using gas-liquid chromatography with flame ionization detection; a preliminary methylation procedure is required for the non-volatile acids prior to analysis. However, it was soon discovered that this method had serious shortcomings. Considerable hydrolysis of the ethyl acetate apparently occurred during the extraction procedure, and resulted in huge acetic acid peaks in the chromatograms. That this problem was a result of hydrolysis of ethyl

acetate and not contamination is illustrated clearly in Figure 2-8. Injection of just ultrapure ethyl acetate into the gas chromatograph resulted in no indication of acetic acid. However, ultrapure water extracted with the ethyl acetate under the conditions described above and injected into the gas chromatograph resulted in a chromatogram with a huge acetic acid peak. Not only does this obviate the analysis of acetic acid using this method, but the very large acetic acid peak obtained enveloped peaks for a number of other fatty acids as well (see Figure 2-8). The use of other extractants (e.g. tetrahydrofuran and diethyl ether), with the procedure outlined above also resulted in analytical difficulties. Recently, a method for the analysis of low molecular weight fatty acids using high pressure liquid chromatography with ultraviolet (254 nm), detection has been published (Barcelona et al., 1980). However, this approach was not persued at this time.

E. Ultrafiltration

Molecular size distributions of DOC and iron in pore water from Great Bay sediments were determined using ultrafiltration. Ultrafiltration involves the separation of macromolecular substances by filtration under applied hydrostatic pressure, and differs from ordinary filtration only in the size of the material being filtered (Karger et al., 1973). For this study, an Amicon model 52 stirred cell (65 ml volume capacity), and Amicon Diaflo type XM-50, PM-10 and UM-02 filter membranes were used (Amicon Corporation, Lexington, Massachusetts). The membranes are made from a non-cellulosic polymer, and consist of a thin skin of controlled pore size on an open-celled, spongy layer of this same material. The separation is accomplished by the thin skin. The XM-50, PM-10 and UM-02 membranes have nominal molecular weight cut-

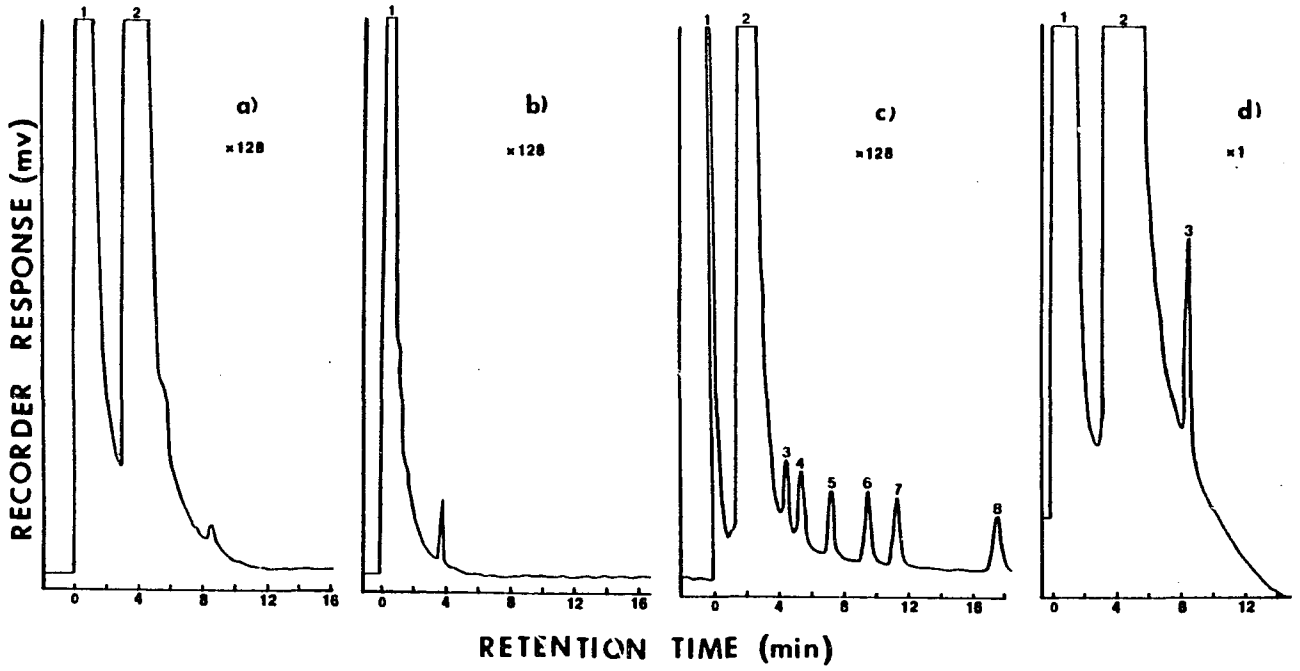

Figure 2-8. Gas-liquid chromatograms for low molecular weight fatty acids method: a) ultrapure water extracted with ethyl acetate (1 = solvent peak, 2 = acetic acid); b) ethyl acetate only (1 = solvent peak); c) volatile fatty acid mixture @ 1 mM each extracted with ethyl acetate (1 = solvent peak, 2 = acetic acid envelope, 3 = n-butyric acid, 4 = isovaleric acid, 5 = n-valeric acid, 6 = isocaproic acid, 7 = n-caproic acid, 8 = heptanoic acid); d) pore water sample (0-2 cm section, Site 3), extracted with ethyl acetate (1 = solvent peak, 2 = acetic acid envelope, 3 = n-valeric or isocaproic acid). Note the higher sensitivity in chromatogram d, (e.g. x 1 versus x 128 in the other chromatograms). The chromatographic conditions were: N_2 carrier flow of 30 ml/min; FID temperature of 170°C; injector temperature 150°C; and the column temperature programmed from 130°C to 190°C at 8°C/min. A Supelco (Bellefonte, Pa.), SP-1200 column (4mm x 2m), was used for the separation.

offs of 50,000, 10,000 and 1,000, respectively. Both the XM-50 and PM-10 membranes are non-ionic, while the UM-02 membranes are anionic in character. Care was exercised to remove the glycerol coating on the membranes (added to stabilize the membranes during storage). The cleaning procedure consisted of soaking the filters in 10% W/V NaCl solution for 48 hours, followed by placing the membranes in the cell and flushing the system with at least 400 ml of 10% W/V NaCl solution and finally 100 ml of D/D water. The apparatus itself was soaked overnight in 10% V/V HCl and thoroughly rinsed with D/D water prior to use. Corrections for contamination were made by running known volumes of D/D water through the ultrafiltration system, and determining DOC and iron concentrations in these blanks. Quantitative recoveries of both DOC and iron standards with molecular weights less than the stated cutoff values of the various membranes were attained.

The general ultrafiltration scheme used experimentally in this study is illustrated in Figure 2-9. A cascade type flow scheme was followed to avoid clogging of the filters and concentration polarization (Smith, 1976). The ultrafiltration cells were pressurized with nitrogen gas at pressures of 20 psi, 10 psi and 50 psi for the XM-50, PM-10 and UM-02 membranes, respectively. These pressures resulted in corresponding flow rates of 10, 8 and 2 ml/min. Membranes were discarded when large deviations from these flow rates were observed or when visible tears in the membrane skin were observed. Used membranes were stored in 10% V/V ethanol-water at $4^{o}C$. All ultrafiltration of pore water samples was carried out in a glove bag under nitrogen in order to avoid oxidation artifacts (see Chapter 3). At least 2 ml of each pore water

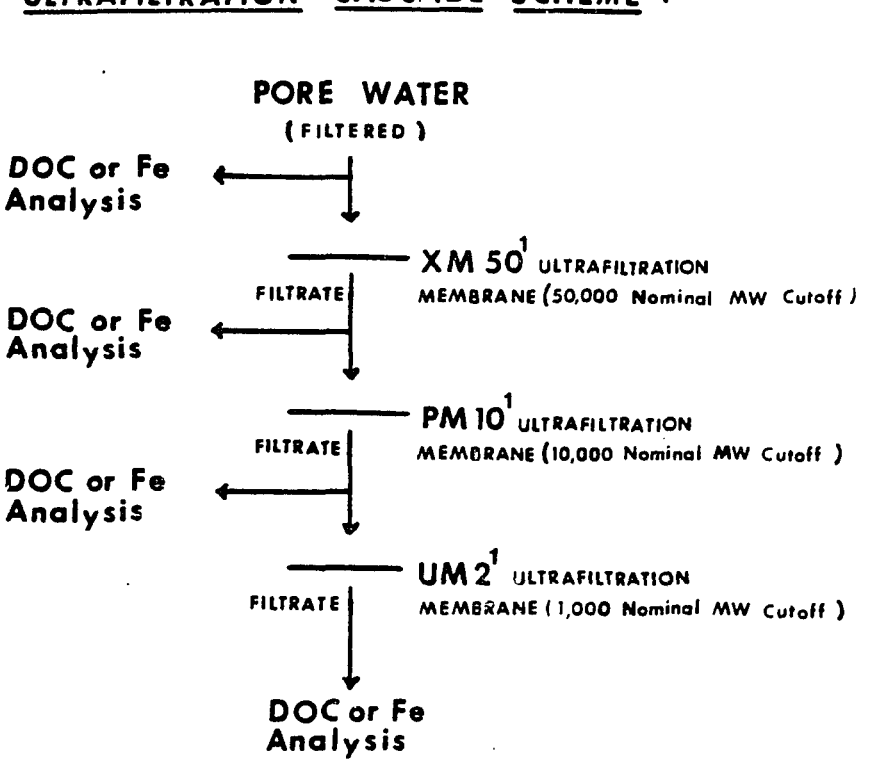

Figure 2-9. General experimental flow scheme for the ultrafiltration of anoxic pore water for DOC and iron analysis.

sample was run through each ultrafiltration membrane and discarded, prior to the collection of a sample for analysis. Ultrafiltered samples for DOC analysis were collected in prebaked (450°C), glass vials and stored as previously described. Ultrafiltered iron samples were collected in precleaned plastic bottles and stored as described earlier. The percentages of DOC and iron in each size class were calculated by dividing the concentrations of these species in each molecular weight range by their total concentrations in the pore water.

F. High Pressure Liquid Chromatography

Reversed phase high pressure liquid chromatography (HPLC), was used: 1) to evaluate the general polarity and homogeneity of organic matter in anoxic pore water and 2) to fractionate this material for spectroscopic analysis. A Waters Associates model ALC/GPC 202 HPLC with a U6K injector coil (Waters Associates, Milford, Massachusetts), was employed for this work. Both a 254 nm differential UV detector and a model 401 differential refractometer were used to monitor the HPLC effluent. However, refractive index detection proved to be much less sensitive for the identification of different fractions of dissolved organic matter than ultraviolet absorption, and was not used after preliminary work. Separation of the dissolved organic matter was accomplished using a Waters C-18 10 μ-Porasil-B semi-preparative column (4 m x 10 mm). Injection volumes ranged from 1.0 to 2.0 ml. All solvents used for preparing the mobile phase (methanol, n-propanol, acetonitrile and water), were of HPLC grade from Fisher Scientific (Boston, Mass.). Solvents were bubbled with N_2 gas for 30 minutes prior to use in order to remove dissolved oxygen, and avoid oxidation of the dissolved organic matter during the separation. Following this, the solvents were

filtered through Millipore membranes (0.2 μm pore size and 47 mm diameter); fluoropore filters for acetonitrile and celotate filters for all the other solvents. The filtering procedure served to remove particles and as an initial degassing step. Final degassing of the solvents was accomplished by sonication for periods of up to one hour.

This study represents a first attempt at the use of HPLC for the separation of the mixture of organic components in anoxic marine pore water. As such, a solvent system for use as a mobile phase had to be developed and optimized. Solvent systems for the separation of organic matter extracted from anoxic marine sediments by HPLC had been previously developed by Templeton (1980), and Lammela (1981); and were used as starting points in this study. The different solvent systems studied are presented in Table 2-3. Lammela (1981), observed a ternary system of water/alcohol/acetonitrile to provide adequate resolution of organic matter extracted from marine sediments; and to be far superior to any binary systems tested. Based on this observation, only ternary systems were investigated here. Figures 2-10 and 2-11 illustrate the effect of increasing n-propanol and acetonitrile compositions in the mobile phase on the separation of the dissolved organic matter. For the sample from the top 15 cm of sediment, (Figure 2-10), optimum resolution was achieved at a mobile phase composition of 80% water/10% n-propanol/10% acetonitrile. At a composition of 100% water, only one fairly sharp peak was observed in the chromatogram at an elution time of about 13.5 minutes. Gradual increases in the n-propanol and acetonitrile percentages in the mobile phase had the effect of 'smearing-out' this peak in the direction of the void volume. A similar effect was seen in the pore water sample from the 45-60 cm section (Figure 2-11).

Table 2-3. Solvent systems tested for HPLC optimization.

Flow (ml/min)	Water (%)	n-propanol (%)	Methanol (%)	Acetonitrile (%)
4	100	-	0	0
4	90	-	5	5 **
4	80	-	10	10 *
4	70	-	15	15
4	60	-	20	20
4	100	0	-	0
4	90	5	-	5
4	80	10	-	10
4	70	15	-	15
4	60	20	-	20
2	100	0	-	0
2	90	5	-	5
2	80	10	-	10
2	70	15	-	15
2	60	20	-	20

all % on a V/V basis

* optimum composition for 0-15 cm core section

** optimum composition for 45-60 cm core section

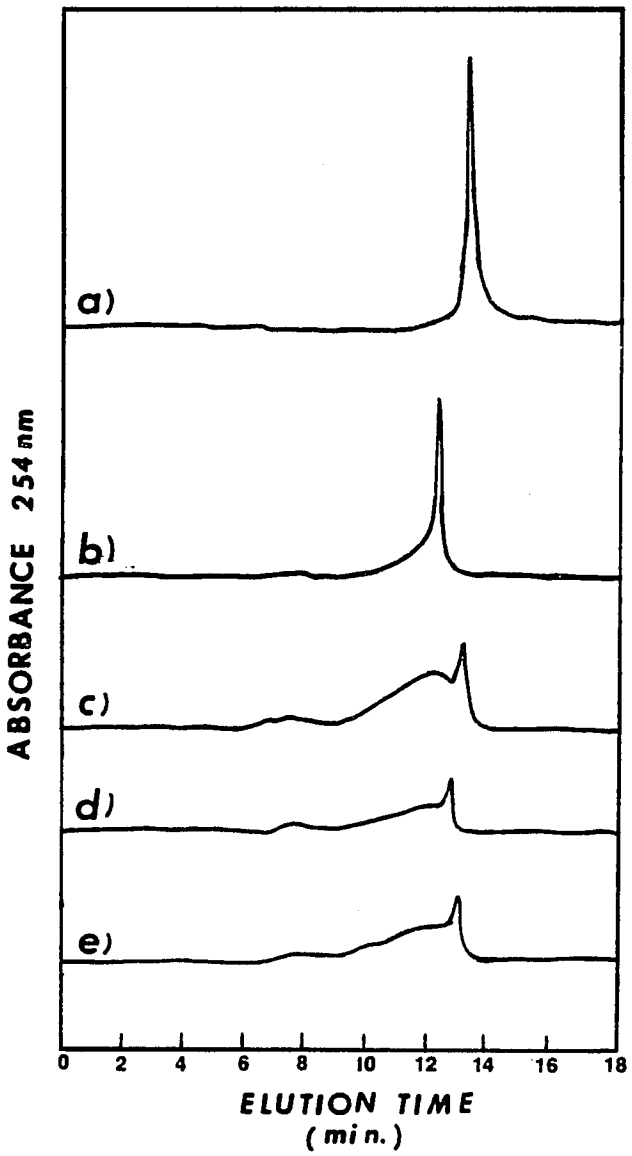

Figure 2-10. High pressure liquid chromatograms of pore water organic matter (0-15 cm section of core from Site 4), showing the effect of different mobile phases on the separation: a) 100% water; b) 90% water/5% n-propanol/5% acetonitrile; c) 80% water/10% n-propanol/10% acetonitrile; d) 75% water/15% n-propanol/15% acetonitrile; and e) 60% water/ 20% n-propanol/20% acetonitrile. Flow rate was 4 ml/min, column C-18 10 μ-Porasil B (4m x 10 mm), injection volume was 1.0 ml.

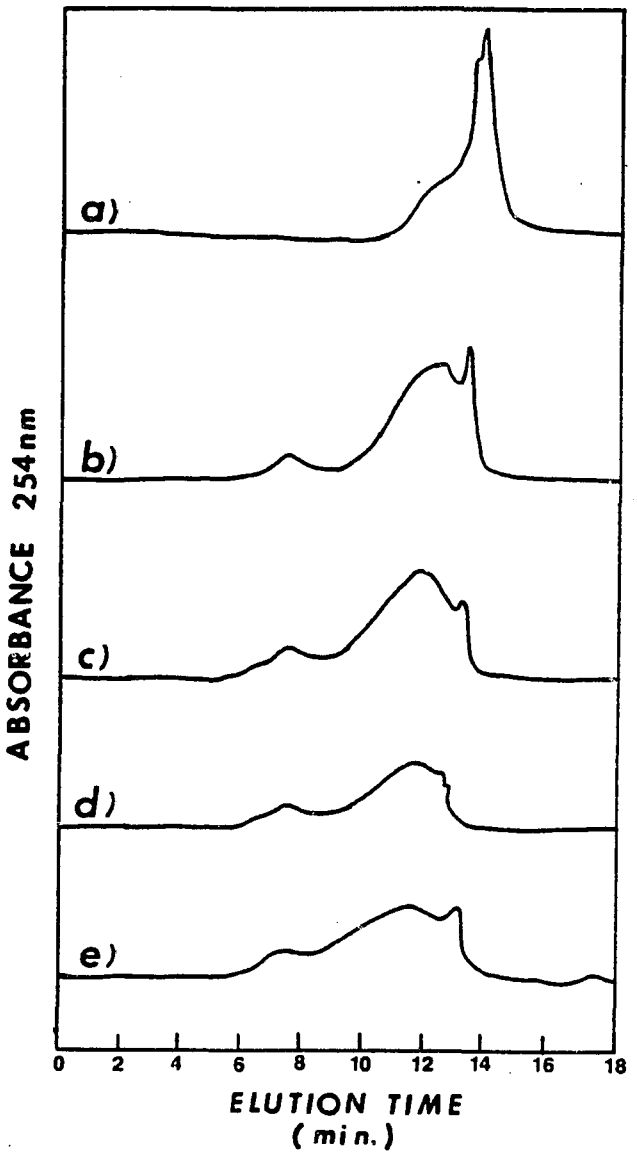

Figure 2-11. High pressure liquid chromatograms of pore water organic matter (45-60 cm section of core from Site 4), showing the effect of different mobile phases on the separation: a) 100% water; b) 90% water/5% n-propanol/5% acetonitrile; c) 80% water/ 10% n-propanol/10% acetonitrile; d) 75% water/15% n-propanol/15% acetonitrile; and e) 60% water/ 20% n-propanol/20% acetonitrile. Other conditions the same as in Figure 2-10.

However, optimum resolution here was achieved at a mobile phase composition of 90% water/5% n-propanol/5% acetonitrile. This was surprising, as it was expected that dissolved organic matter in the deeper sections of the core would be less polar and require a higher percentage of acetonitrile and n-propanol in the mobile phase, compared to organic matter in pore water from surficial sediments. Lammela (1981), obtained optimum resolution of sedimentary organic matter with a mobile phase composition of 60% water/20% n-propanol/20% acetonitrile. This suggests an overall lower polarity of sedimentary organic matter compared to organic matter dissolved in pore water as suggest by Nissenbaum and Kaplan (1972). The substitution of methanol for n-propanol had little effect on the separation. Similarly, changes in the flow rate were observed to have no significant effect on the resolution obtainable with these compositions of mobile phase. Obviously, the compositions of mobile phase termed optimum above do not necessarily represent the ultimate for the fractionation of organic matter from anoxic marine pore water, since only a limited number of systems were tested. Indeed, the above study was entirely limited to isocratic systems, due to a lack of gradient elution capability on the instrument available. However, the solvent system developed here represents a workable system for the fractionation of pore water organic matter.

G. Spectroscopic Studies

Spectroscopic studies of the organic matter in anoxic marine pore water were carried out in order to attempt to delineate some of the structural characteristics of this material. This included analysis of the bulk dissolved organic matter, as well as various fractions of this material separated by HPLC. Measurements carried out included ultra-

violet/visible absorption and fluorescence. Preliminary studies of this material using infrared absorption and nuclear magnetic resonance were unsuccessful for two reasons: 1) the complexity of the bulk organic matter (resulting in uninterpretable spectra), and 2) low concentrations of organic matter in the various fractions from the HPLC.

Ultraviolet/visible absorption spectroscopy was carried out using a Cary 219 Spectrophotometer (Varian Associates, Palo Alto, California). Scans were normally carried out over a wavelength range of 700 to 220 nm, with an absorbance of 0 to 2 full scale. Fluorescence measurements were performed using a Perkin-Elmer 204 Fluorescence Spectrophotometer. In this study, three excitation wavelengths were examined, based on the work of Ewald (1976): 370 nm, 264 nm and 250 nm. Fluorescence emission was scanned over a wavelength range of 780 to 220 nm. Corrections for Rayleigh, Raman and Tyndall scattering were made as recommended by Ewald (1976). Infrared absorption measurements were made with a Perkin-Elmer 283B Infrared Spectrophotometer over a frequency range of 4,000 to 600 cm^{-1}. Sample for infrared analysis were prepared by freeze-drying and pressing into KBr pellets. Nuclear magnetic resonance measurements were made using a high-resolution, JEOL FX-90Q Pulse Fourier-Transform NMR Spectrometer (JEOL Ltd., Tokyo, Japan), equipped with digital quadrature detection, a multinuclear broadband probe (H^1 and C^{13} were used in this study), variable temperature accessory and foreground/background data manipulation software. The techniques used for nuclear magnetic resonance analysis of the dissolved organic matter were similar to those employed by Templeton (1980).

Care was exercised in all spectroscopic studies of pore water

organic matter to avoid oxidation of this material as a result of exposure to atmospheric oxygen (see Chapter 3). Transfer of samples to cuvettes or NMR tubes was carried out in a glove bag under an N_2 atmosphere, and the cuvettes and NMR tubes were securely capped before removal to the laboratory atmosphere for analysis. Dissolved organic matter fractions from the HPLC were collected for spectroscopic analysis under anoxic conditions in a glove bag. Pore water samples were stored under N_2 in a glove bag and fixed with 0.1 M sodium azide to retard bacterial action, prior to spectroscopic analysis as mentioned earlier.

Appropriate blank corrections were made for all spectroscopic studies. This was of particular importance for the fractions collected from the HPLC, in that the ultraviolet/visible absorption and fluorescence of the mobile phase had to be subtracted from the spectra obtained.

V. Analytical Reproducibility

The reproducibility of the various analytical methods used in this study was determined by the analysis of a number of replicates of a pore water or sediment sample. The use of a pore water or sediment sample for this determination, as opposed to using standard solutions, was appropriate in order to simulate as closely as possible matrix effects that may affect the analysis of actual samples. The results of these determinations are presented in Table 2-4. In this table, the number of replicates, the mean value for these replicates ($\bar{x}$), the standard deviation (s), and the % relative standard deviation (% RSD), for each analytical method are presented. The number of replicates used for estimating the analytical reproducibility of an individual method varied

Table 2-4. Analytical reproducibility.

	Analysis	No. Replicates	$\bar{X}$[a]	S[b]	% RSD[c]
1)	Sediment Size (%)	3			
	a) Sand		49.27	3.45	7.00
	b) Silt		41.68	3.47	8.33
	c) Clay		9.043	0.489	5.41
2)	Sedimentary Organic Carbon (%)	8	2.15	0.41	19
3)	Sedimentary Organic Nitrogen (%)	8	0.21	0.03	14
4)	Sedimentary Organic Phosphorus (ppm)	8	2.6	0.5	19
5)	Sedimentary Inorganic Phosphorus (ppm)	8	14.9	0.6	4
6)	pH	10	7.46	0.12	1.6
7)	Titration Alkalinity (meq/l)	10	12.63	0.11	0.87
8)	Chloride ($^{o}/_{oo}$)	15	13.4	0.05	0.4
9)	Sulphate (m$\underline{M}$)				
	a) gravimetric method	5	20.0	0.4	2
	b) titrimetric method	12	17.4	0.0759	0.436
10)	Ammonia (μ$\underline{M}$)	15	93.3	1.45	1.55
11)	Phosphate (μ$\underline{M}$)	15	8.95	0.065	0.73
12)	Silicate (μ$\underline{M}$)	15	178	3.55	1.99
13)	Total Iron (ppm)	12	6.81	0.09	1
14)	Dissolved Organic Carbon (mgC/l)	24	2.1	0.3	15
		36	31.5	1.2	3.8
		10	65.8	0.7	1.1
15)	Amino Acids (μgN/l)	10	44.2	1.2	2.7
16)	Carbohydrates (μg/l)	10	1020	40	3.9

Table 2-4. continued.

Analysis	No. Replicates	$\bar{X}$[a]	S[b]	% RSD[c]
17) Ultrafiltration of Dissolved Organic Carbon (mgC/l)				
a) XM-50	4	30.8	3.1	10
b) PM-10	4	21.1	2.5	12
c) UM-2	4	2.5	0.4	16

a) $\bar{X}$ = mean, $\bar{X} = (\sum_{i=1}^{n} X_i)/n$.

b) S = standard deviation, $S = \sqrt{(\sum_{i=1}^{n} (X_i-\bar{X})^2)/(n-1)}$.

c) % RSD = $(S/\bar{X}) \cdot 100$.

from as many as 36 to 3. The relatively few replicates run for sediment size analysis and dissolved organic carbon ultrafiltration were a consequence of sample and equipment limitations.

In general, % RSD's for individual analytical methods used in this study were similar to those obtained by other investigators in work with anoxic marine pore water. The relatively poor precisions observed for some sediment analyses probably reflect large inhomogeneities in the sample, even after grinding to achieve a relatively homogeneous sample. The dramatic increase in the % RSD of the DOC analysis with decreasing concentration was of interest, although not totally unexpected. The manufacturer states a reproducibility of 5% above 1 mgC/l and 10% below this level of DOC. As shown in Table 2-4, the observed precision of this instrument for pore water was actually somewhat better than this at DOC concentration of about 66 and 31 mgC/l. However, at a concentration of about 2 mgC/l, the reproducibility of this instrument in pore water was significantly less than the manufacturer's estimate; possibly as a consequence of the largely colloidal nature of the DOC in pore water (see Chapter 5). The overall precision of the ultrafiltration technique as applied to the molecular weight fractionation of DOC in pore water was considerably better than that determined by Smith (1976), for open ocean and nearshore seawater samples. This is probably attributable to two factors: 1) the higher concentrations of DOC in pore water relative to seawater and 2) the superior precision of the PHOTOchem organic carbon analyzer compared to the persulphate oxidation method (Menzel and Vacarro, 1964), used by Smith (1976).

In later chapters, statements concerning significant differences

between individual points in a depth profile of a core will be based on the estimates of reproducibility presented in Table 2-4. Although many of the points presented in these depth profiles represent averages of duplicates or triplicates, the estimates of reproducibility given in Table 2-4 probably represent a closer approximation to the true analytical precision (s), than duplicates or triplicates of individual points. Error bars will not be presented in plots in the following chapters for reasons of clarity of data presentation. Rather, discussions of the significance of various trends will be treated in the text.

VI. Spatial Variability

An estimate of the spatial variability of a number of chemical species at Site 4 in Great Bay was obtained by taking two gravity cores side by side on a single sampling date. It was originally planned to take five gravity cores in a cross pattern at this site on a single sampling date. However, due to manpower and equipment limitations, it was found that only two cores at a time could be handled with confidence to obtain representative samples with no oxidation effects (see Chapter 3). One of the goals of this study was an investigation of the temporal variations in the concentrations of a number of chemical species in Great Bay pore water. As such, it was necessary to establish that the observed temporal variations were not simply an artifact of spatial inhomogeneities.

The spatial variabilities for a number of inorganic species at this site are presented in Table 2-5. Ranges of % RSD's were: pH (0.2% to 2%); titration alkalinity (0.4% to 6%); chloride (o% to 2%); sulphate (6% to 87%); ammonia (0.8% to 41%); phosphate (0.4% to 23%); silicate (0% to 26%); iron <0.45 μm (0% to 21%); and iron <1.0 μm (8% to 64%). In

Table 2-5. Spatial variability (inorganic species)

Cores OAX-I and CMP-I
Site 4 (Footman Islands)
Date: 6-23-80

Depth (cm)	pH		Alkalinity (meq/l)	
	OAX-I	CMP-I	OAX-I	CMP-I
0-15	7.33	7.24	3.88	3.81
15-30	7.47	7.26	8.57	8.50
30-45	7.35	7.38	15.28	17.78
45-60	7.64	7.27	22.71	23.52
60-75	7.60	7.28	26.90	25.98
75-90	7.50	7.24	27.42	28.62

Depth (cm)	Chloride (°/oo)		Sulphate (mM)	
	OAX-I	CMP-I	OAX-I	CMP-I
0-15	13.4	14.0	18.5	23.5
15-30	13.7	13.6	14.4	25.5
30-45	13.7	13.7	12.6	14.1
45-60	13.8	13.5	6.0	8.3
60-75	13.7	13.5	0.3	4.6
75-90	13.4	13.5	0.2	-

Depth (cm)	Ammonia (µM)		Phosphate (µM)	
	OAX-I	CMP-I	OAX-I	CMP-I
0-15	44.7	107	27.7	44.5
15-30	263	259	86.5	84.0
30-45	561	573	132	124
45-60	529	605	103	118
60-75	577	701	120	112
75-90	701	726	112	111

Table 2-5. continued.

Depth (cm)	Silicate (μM) OAX-I	Silicate (μM) CMP-I	Iron (ppm)[1] OAX-I	Iron (ppm)[1] CMP-I
0-15	83.8	109	0.24	0.37
15-30	80.0	73.8	-	0.24
30-45	93.4	159	0.15	0.20
45-60	68.0	85.3	0.27	0.20
60-75	56.3	56.3	0.17	0.17
75-90	66.6	85.3	0.12	0.21

Depth (cm)	Iron (ppm)[2] OAX-I	Iron (ppm)[2] CMP-I
0-15	0.65	0.89
15-30	0.64	3.01
30-45	0.66	1.33
45-60	0.83	0.97
60-75	0.54	2.09
75-90	2.10	1.37

1) Filtered through 0.5 μm Nuclepore filters.

2) Filtered through 1.0 μm Whatman GF/C filters.

general, variations were greatest in the surficial sediments, particularly for biochemically active ions such as ammonia and phosphate. This is probably a consequence of spatial variability in bacterial activities at this sampling location. In addition, bioturbation may be a factor in the lateral variability observed in surficial sediments. The relatively high variability of dissolved iron in both size classes is probably due to the colloidal character (see Chapter 4), and complex speciation of this element in anoxic marine pore water. The large variation in sulphate concentration between the two cores may reflect spatial inhomogeneities in sulphate reduction activities as well as the complex chemistry of sulphur in anoxic sediments. Besides actual differences in the pore water composition between the two cores, a portion of the observed spatial variability probably resulted from differential vertical compaction of the cores during sampling. Despite the quantitative differences exhibited between the two cores for these chemical species, qualitative depth profiles for most of these species were remarkably similar.

The spatial variability of DOC at Site 4 in Great Bay is presented in Table 2-6 for duplicate sets of cores obtained on two different sampling dates. Percentage RSD values ranged from 2% to 14% for the cores obtained in June and 4% to 16% for the cores obtained in October. As with many of the biochemically active inorganic species, the largest spatial variability in DOC concentration was observed in the upper sections of sediment. Spatial variability in DOC concentrations is undoubtably linked to variations in bacterial activities at a sampling location, as well as bioturbation. The two cores from each sampling date in Table 2-6 exhibited qualitatively similar depth pro-

Table 2-6. Spatial variability (DOC).

Cores OAX-I and CMP-I
Site 4 (Footman Islands)
Date: 6-23-80

Depth (cm)	DOC (mgC/l) OAX-I	CMP-I	% RSD
0-15	14.3	11.9	9.1
15-30	29.1	22.7	12.4
30-45	46.5	34.8	14.4
45-60	46.7	41.5	5.9
60-75	46.1	44.6	1.7
75-90	50.1	41.9	8.9

Cores OAX-II and UF-VIII
Site 4 (Footman Islands)
Date: 10-21-80

Depth (cm)	DOC (mgC/l) OAX-II	UF-VIII	% RSD
0-15	19.5	14.1	16.1
15-30	22.1	29.4	14.1
30-45	33.4	38.7	7.3
45-60	42.1	38.9	3.9
60-75	43.3	39.4	4.7
75-90	-	41.9	-

files for DOC.

Table 2-7 presents the spatial variability of the molecular size distribution of DOC in the same two cores from the June 23, 1980 cruise at Site 4 as discussed above for inorganic species and DOC concentration. Percentage RSD's ranged from 0.2% to 28% for these two cores. This was considerably lower than expected, considering the analytical variability expected with the ultrafiltration technique (see Table 2-4); and represents a good illustration of the consistent colloidal nature of organic matter in anoxic marine pore water which is discussed in much greater detail in Chapter 5.

Table 2-7. Spatial variability (DOC) ultrafiltration).

Cores OAX-I and CMP-I
Site 4 (Footman Islands)
Date: 6-23-80

Depth (cm)	Total DOC (mgC/l)		DOC > 1,000 MW (mgC/l)		DOC < 1,000 MW (mgC/l)	
	OAX-I	CMP-I	OAX-I	CMP-I	OAX-I	CMP-I
0-15	14.3	11.9	9.6	8.8	4.7	3.1
15-30	29.1	22.7	24.7	13.8	4.4	8.9
30-45	46.5	34.8	41.3	23.3	5.2	11.5
45-60	46.7	41.5	39.6	32.6	7.1	8.9
60-75	46.1	44.6	41.1	41.3	5.0	3.3
75-90	50.1	41.9	46.5	34.4	3.6	7.5

Depth (cm)	DOC > 1,000 MW (%)		DOC < 1,000 MW (%)	
	OAX-I	CMP-I	OAX-I	CMP-I
0-15	67.2	73.9	32.8	26.1
15-30	84.9	60.8	15.1	39.2
30-45	88.8	66.9	11.2	33.1
45-60	84.8	78.5	15.2	21.5
60-75	89.1	92.6	10.8	7.4
75-90	92.8	82.1	7.2	17.9

CHAPTER 3

PORE WATER FROM ANOXIC MARINE SEDIMENTS: OXIDATION EFFECTS

I. Introduction to Problem

As discussed in Chapter 1, one of the principal aims of this study was to investigate the validity of chemical data obtained from anoxic marine pore water, especially with regard to organic species. Previous workers have shown that in handling pore water extracted from anoxic marine sediments, failure to maintain in situ sediment temperatures results in changes in the concentrations of a number of chemical species (Mangelsdorf et al., 1969; Bischoff et al., 1970; Fanning and Pilson, 1971; and Hulbert and Brindle, 1974). However, the direction of these concentration changes was observed to vary, depending on the ion. For example, enrichment of K^+, Cl^- and SiO_4^{4-} ions in the pore water of sediments warmed from in situ temperature conditions was observed; while depletion of Mg^{2+} and Ca^{2+} in the pore water occurred under these same handling conditions (Bischoff et al., 1970; and Fanning and Pilson, 1971). These compositional changes in the pore water were thought to be a result of temperature induced shifts in the ion exchange equilibria of the pore water/sediment system (Mangelsdorf et al., 1969; and Bischoff et al., 1970), although other explanations are also possible (Fanning and Pilson, 1971; and Hulbert and Brindle, 1974). Moreover, it has been suggested that the magnitude of these temperature effects may depend strongly on a number of interacting variables, especially

the type of clay mineral dominant in the sediment. The potential effects of these temperature induced sample handling artifacts on other inorganic ions and on dissolved organic matter in anoxic pore water is unknown, however, it is probably best to maintain in situ temperature conditions when possible during processing.

More recently, the effects of exposure of originally anoxic sediments to atmospheric oxygen during sample processing on the concentrations of PO_4^{3-}, SiO_4^{4-} and total dissolved iron in pore water have been investigated (Bray et al., 1973; Troup et al., 1974; Loder et al., 1978; and Lyons et al., 1979d). The results of these studies have shown oxidation to result in decreases in the concentrations of all of these species in the pore water from both clastic and carbonate sediments. The mechanism of iron removal has been hypothesized to proceed via oxidation of Fe^{2+} to Fe^{3+}; with the subsequent formation of insoluble iron(III) oxi-hydroxides. Phosphate and SiO_4^{4-} ions were thought to be removed by co-precipitation, either adsorbed or occluded in the iron(III) phosphate and silicate minerals is also possible (Bray et al., 1973; and Loder et al., 1978). Loder and co-workers (1978), have also suggested that since iron(III) oxi-hydroxides are noted scavangers of many trace metals (Jenne, 1968), as well as dissolved organic materials (Williams and Zirino, 1964), in seawater, these may also be removed from pore water as a result of oxidation during handling. However, no study of this has yet been undertaken.

The major focus of this dissertation has been to elucidate some of the properties of and processes affecting organic matter in the pore water of anoxic estuarine sediments. However, from the discussion above, a systematic study of the effects of sample handling on the dis-

solved organic matter in pore water was necessary, prior to proceeding with this larger work. The study presented in this chapter had three major objectives:

1) To evaluate the effects of oxidation during sample handling on the concentration of dissolved organic carbon in pore water from anoxic marine sediments;

2) To determine any changes oxidation of the pore water may have on the nature of the dissolved organic matter;

3) To reevaluate the oxidation effects observed by previous workers.

These results, as well as some other aspects of sample handling and storage of anoxic pore water are presented below.

The approach taken to evaluate these oxidation effects was similar to that of Loder et al. (1978). A number of both box and gravity cores were obtained from Sites 3 and 4 in the Great Bay Estuary by procedures outlined in Chapter 2. Processing of these cores was also carried out as described in Chapter 2, except that approximately half of each core section was removed from the glove bag (following the homogenization process), and exposed to the laboratory atmosphere for the centrifugation and filtering procedures (about 1½ hours). Strict anoxic conditions were maintained on the other half of each core section, and care was taken to assure that the two halves from each core section were handled similarly, except for degree of exposure to atmospheric oxygen. All analyses performed were as described in Chapter 2.

II. Results and Discussion

A. Effects of Oxidation on Inorganic Species

Titration Alkalinity and pH. Results of oxidation effects on the measured values of titration alkalinity from one box and two grav-

ity cores (all from Site 4), are presented in Table 3-1. These data are illustrated in Figure 3-1. With the exception of the 2-4 cm section in core OAX-A, all titration alkalinity values are lower in the samples exposed to atmospheric oxygen. Percentage alkalinity losses as a result of oxidation ranged from 5% up to as much as 63%. Average percentage losses were 37% for core OAX-A, and 13% and 21% for cores OAX-I and OAX-II, respectively. Absolute alkalinity losses in the oxidized samples ranged from 0.5 meq/l to nearly 5 meq/l. This is the first report of decreases in titration alkalinity values as a result of exposure of anoxic sediments to atmospheric oxygen. A similar set of experiments in Bermuda carbonate sediments conducted by Lyons and co-workers (1979d), showed no significant difference in the alkalinities of nitrogen processed and oxygen exposed sediment samples. The discrepancy between the results of these researchers and those presented here may be due to environmental differences between Great Bay clastic and Bermuda carbonate sediments. In addition, differences in oxygen exposure times between these two studies may also be a factor.

The major contributor to the alkalinity of anoxic pore water is the bicarbonate ion; with lesser contributions from phosphate, ammonia and bisulphide ions and from dissolved organic acids (Berner et al., 1970; and Gieskes and Rogers, 1973). Thus, any process tending to reduce the concentrations of these species in the pore water would simultaneously reduce alkalinity values. Removal of HCO_3^- or CO_3^{2-} from the pore water either by precipitation as a mineral phase or co-precipitation on an amorphous colloid (e.g. as on iron (III) oxi-hydroxides produced following oxidation of the pore water), might account for the lower alkalinities observed in the oxidized samples. However, no supportive

Table 3-1. Effects of oxidation of pore water on measured values of titration alkalinity.

Core OAX-A
Date: 7-23-79
Site 4 (Footman Islands)

Depth (cm)	Anoxic Alkalinity (meq/l)	Oxic Alkalinity (meq/l)
0-2	3.35	2.81
2-4	3.11	3.53
4-6	3.47	2.43
6-8	4.64	1.70
8-10	4.29	2.57
10-12	3.31	2.16

Core OAX-I
Date: 6-23-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic Alkalinity (meq/l)	Oxic Alkalinity (meq/l)
0-15	3.88	3.30
15-30	8.56	7.23
30-45	15.3	14.5
45-60	22.7	19.9
60-75	26.9	23.4
75-90	27.4	22.7

Core OAX-II
Date: 10-21-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic Alkalinity (meq/l)	Oxic Alkalinity (meq/l)
0-15	5.69	3.77
15-30	-	7./1
30-45	17.1	14.1
45-60	22.5	18.7
60-75	27.2	23.3

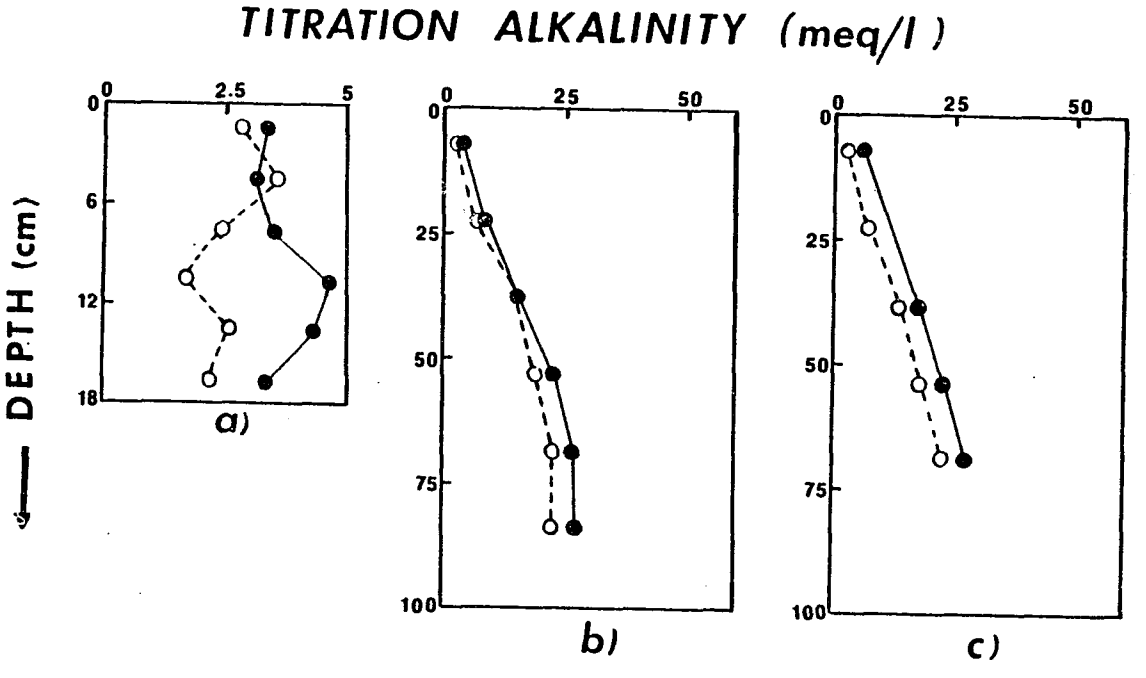

Figure 3-1. Titration alkalinity values (meq/l), plotted versus depth (cm), for the cores from Table 3-1: a) Core OAX-A, Site 4 (7-23-79); b) Core OAX-I, Site 4 (6-23-80); c) Core OAX-II, Site 4 (10-21-80). For each core, pore water processed under anoxic (●—●), and under oxic (o - - o) conditions are plotted side by side.

evidence for either of these processes exists. Loss of CO_2 by degassing from the pore water during sample processing is probably occurring, as evidenced by the pH measurement problem discussed below; however, this would have no effect on alkalinity values (Stumm and Morgan, 1970). Other factors which could contribute to the lower alkalinities observed in the oxidized pore water subsamples include: 1) loss of PO_4^{3-} by co-precipitation with iron(III) oxi-hydroxides following exposure to oxygen (Bray et al., 1973; and Loder et al., 1978), 2) oxidation of ammonia to nitrate (Riley and Chester, 1973), 3) oxidation of reduced sulphur species in the pore water to sulphate (Garrels and Christ, 1965; and Howarth, 1978), and 4) production of acid in the form of H_2SO_4 from the oxidation of elemental sulphur and metal sulphides in the sediments (Stumm and Morgan, 1970; Singer and Stumm, 1970; and Manahan, 1975). Of these factors, the oxidation of reduced sulphur species in the sediments (i.e. process number four above), is likely to have the largest effect. Both phosphate and ammonia concentrations have been observed to decrease upon exposure of anoxic pore water from Great Bay sediments to oxygen (see discussion below). However, these losses cannot account for the large alkalinity decreases observed in some core sections, since together phosphate and ammonia account for less than 2% (on average), of the titration alkalinities in these cores. Indeed, Gieskes and Rogers (1973), have shown that phosphate and ammonia normally contribute less than 3% to the titration alkalinity in anoxic pore waters. The oxidation of reduced sulphur species in pore waters (e.g. HS^- and polysulphides), would not be expected to have an appreciable effect on titration alkalinity values, since even in organic rich sediments the concentration of these species normally does not exceed

1 or 2 m M (Goldhaber and Kaplan, 1974). If the oxidation of elemental sulphur and metal sulphides is, indeed, the process responsible for the lower titration alkalinities in the oxidized pore water samples, concommittant increases in sulphate concentrations in the pore water might be expected. However, as discussed below, no such increases in pore water sulphate concentrations were observed in these cores. One possible explanation for this is that the oxidation of sedimentary elemental sulphur and metal sulphides is incomplete, producing species other than sulphate. The details of this process must await further study.

The pH of anoxic marine pore water has been measured by two different techniques: 1) measurement of the pore water after separation from the sediment and 2) direct insertion of the electrode system into wet sediment samples. A comparison of the pH values obtained using these two techniques on the same core samples is presented in Table 3-2 and illustrated in Figure 3-2. In all cases, pH measurements of the pore water were significantly higher than those determined in the wet sediment. Similar results have been obtained by previous workers (Siever et al., 1961; Garrels and Christ, 1965; Troup, 1974; and Lyons, 1979), and was attributed to degassing of CO_2 from the pore water during the separation procedure. Both squeezing and centrifugation separation processes appear to have similar degassing problems. However, problems may also exist in the measurement of pH by direct insertion into the wet sediment as a result of junction potential effects (Jenney et al., 1950; and Jackson, 1958). In addition, the direct insertion technique usually required long equilibration times to obtain stable readings. Troup (1974), has observed that pore water squeezed directly into a small glass electrode cell under nitrogen results in pH values similar

Table 3-2. Differences in pH values measured on pore water and wet sediment.

Core UF-C
Date 4-26-79
Site 4 (Footman Islands)

Depth (cm)	Sediment pH	Pore Water pH
0-2	7.31	7.60
2-4	7.16	7.76
4-6	7.16	7.75
6-8	7.27	7.86
8-10	7.02	7.82
10-12	7.17	7.83

Core UF-III
Date: 10-30-79
Site 4 (Footman Islands)

Depth (cm)	Sediment pH	Pore Water pH
0-10	7.01	7.69
10-20	7.12	8.04
20-30	7.28	8.08
30-40	7.21	8.22
40-50	7.25	8.38
50-63	7.18	8.54
63-73	7.24	8.08
73-83	7.10	8.04
83-93	7.31	8.01

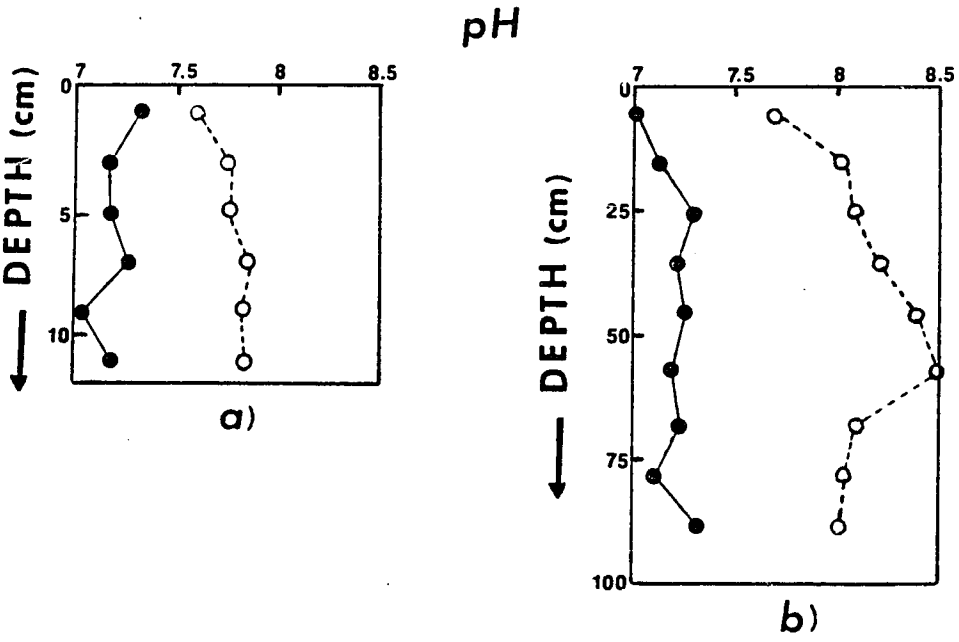

Figure 3-2. pH values plotted as functions of depth (cm), for measurements made on wet sediment (●—●), and pore water (o---o),: a) Core UF-C, Site 4 (4-26-79); and b) Core UF-III, Site 4 (10-30-79).

to those obtained by the direct insertion method. However, for pore water separation techniques requiring longer handling times (e.g. centrifugation, as in this study), measurement of the wet sediment probably results in more accurate pH values.

In addition to the problem of CO_2 degassing during handling, oxidation of the sample may also have a significant effect on the pH of anoxic pore water. In particular, the oxidation of sedimentary elemental sulphur and metal sulphides to produce sulphuric acid in the pore water could greatly influence the pH of this solution. The results of an experiment designed to assess the effects of oxidation on both methods of pH measurement discussed above, are presented in Table 3-3. No significant, systematic effect of oxidation was observed in the samples whose pH was measured by the direct insertion technique, although a significant decrease in titration alkalinity was observed in these samples (note that except for CO_2 degassing which has no effect on alkalinity, processes that effect alkalinity should also effect pH (Stumm and Morgan, 1970)). However, measurements of the pH of the separated pore water of these same samples under oxic and anoxic conditions revealed significantly lower pH values in the oxidized subsamples. The differences between these anoxic and oxic pH values, plotted versus the differences in anoxic/oxic alkalinities for the same core are presented in Figure 3-3. The solid line in the figure represents a linear correlation analysis inclusive of all samples (r^2 = 0.846); while the dashed line is a correlation of the same data, omitting the 0-2 cm core section values (r^2 = 0.974). These results imply that processes causing changes in alkalinity may also be affecting pH values of pore water exposed to oxygen. This is not surprising, since

Table 3-3. Effects of oxidation on the two methods of measuring the pH of anoxic marine sediments.

Core OAX-A
Date: 7-23-79
Site 4 (Footman Islands)

Depth (cm)	Sediment pH		Pore Water pH	
	Anoxic	Oxic	Anoxic	Oxic
0-2	7.18	7.05	7.85	7.85
2-4	7.22	7.29	7.90	7.84
4-6	7.19	7.12	7.99	7.76
6-8	7.17	7.22	8.16	7.59
8-10	7.24	7.19	8.11	7.74
10-12	7.20	7.16	8.02	7.69

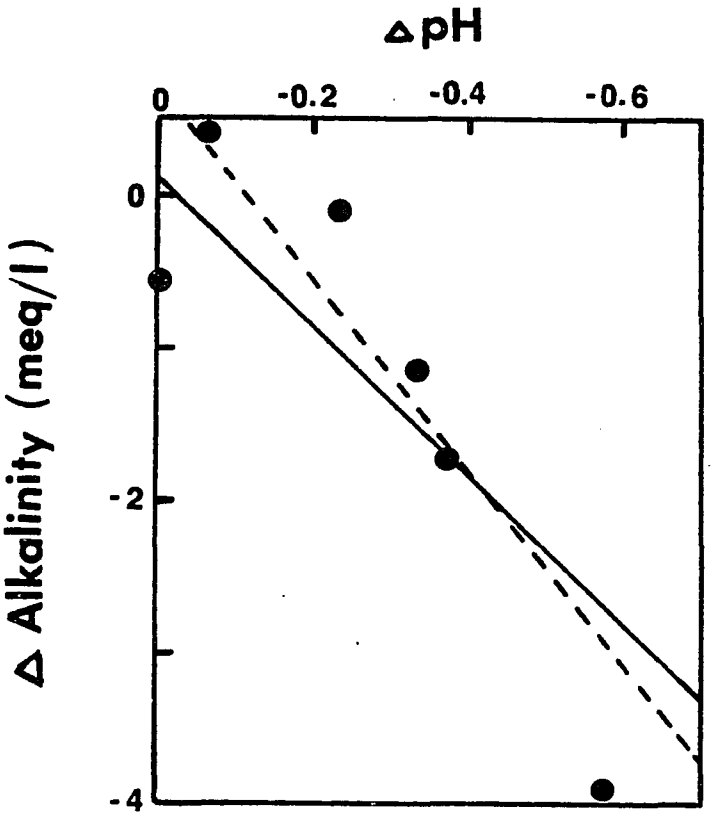

Figure 3-3. Correlation of pH (oxic pH - anoxic pH), and alkalinity (oxic alkalinity - anoxic alkalinity), for core OAX-I. See text for discussion

pH and alkalinity are related quantities (Stumm and Morgan, 1970). The lack of any observable oxidation effect on the pH values measured by the direct insertion technique may be a consequence of two factors: 1) the low permeability of oxygen in wet sediment relative to pore water and 2) the buffering capability of clay minerals (Sillen, 1961; Holland, 1965; Garrels, 1965; and Pytkowicz, 1967). To avoid both degassing of CO_2 and oxidation artifacts, pH measurements in this work were made using the direct insertion technique.

Chloride and Sulphate. Concentrations of chloride ion (°/oo), versus depth for oxic and anoxic subsamples from four different cores are illustrated in Figure 3-4. These results indicate no significant effect of oxidation on Cl^- concentrations in Great Bay anoxic pore water. This is not surprising since Cl^- will not undergo an oxidation state change when exposed to oxygen, and any loss of Cl^- by co-precipitation with iron(III) oxi-hydroxide colloids is unlikely to have a significant impact on the large amounts of Cl^- present in marine pore water.

Similarly, exposure to oxygen had no significant effect on the concentrations of SO_4^{2-} in three Great Bay cores. These data are presented in Figure 3-5. This result was not entirely surprising, considering the high levels of sulphate in marine pore waters (tens of nmoles per liter in surficial sediments), and the much lower levels of reduced sulphur species in the pore water (100 μM to 1 m M (Goldhaber and Kaplan, 1974)). In addition, the lack of any significant increases in the sulphate concentrations of oxidized subsamples may be due to a kinetic effect over the time scale of the experiment, since oxidation HS^- to SO_4^{2-} has been observed during storage of samples under oxic conditions (Howarth, 1978). Indeed, kinetic studies of sulphide oxi-

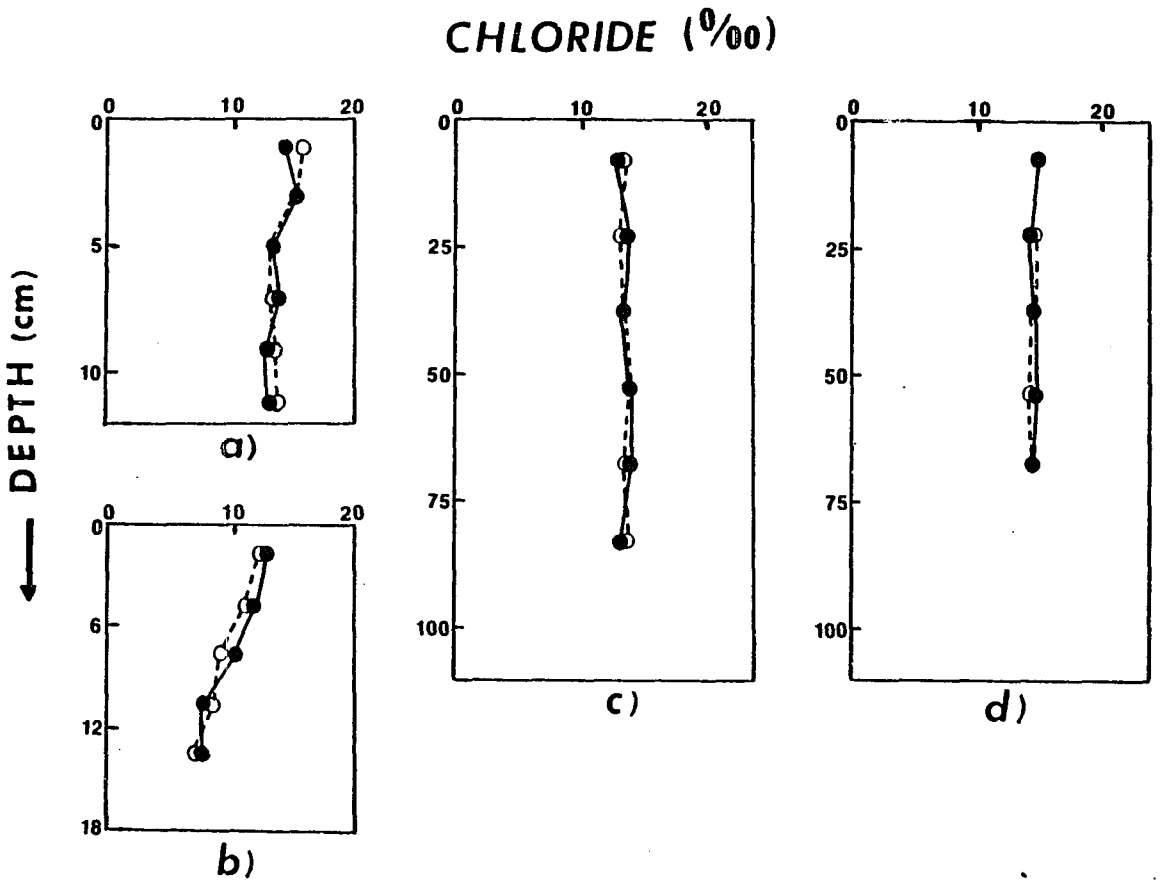

Figure 3-4. Chloride concentrations (‰), versus depth (cm), for oxic (o -- o), and anoxic (●——●), subsamples: a) Core OAX-A, Site 4 (7-23-79); b) Core OAX-B, Site 3 (6-12-80); c) Core OAX-I, Site 4 (6-23-80); and d) Core OAX-II, Site 4 (10-21-80).

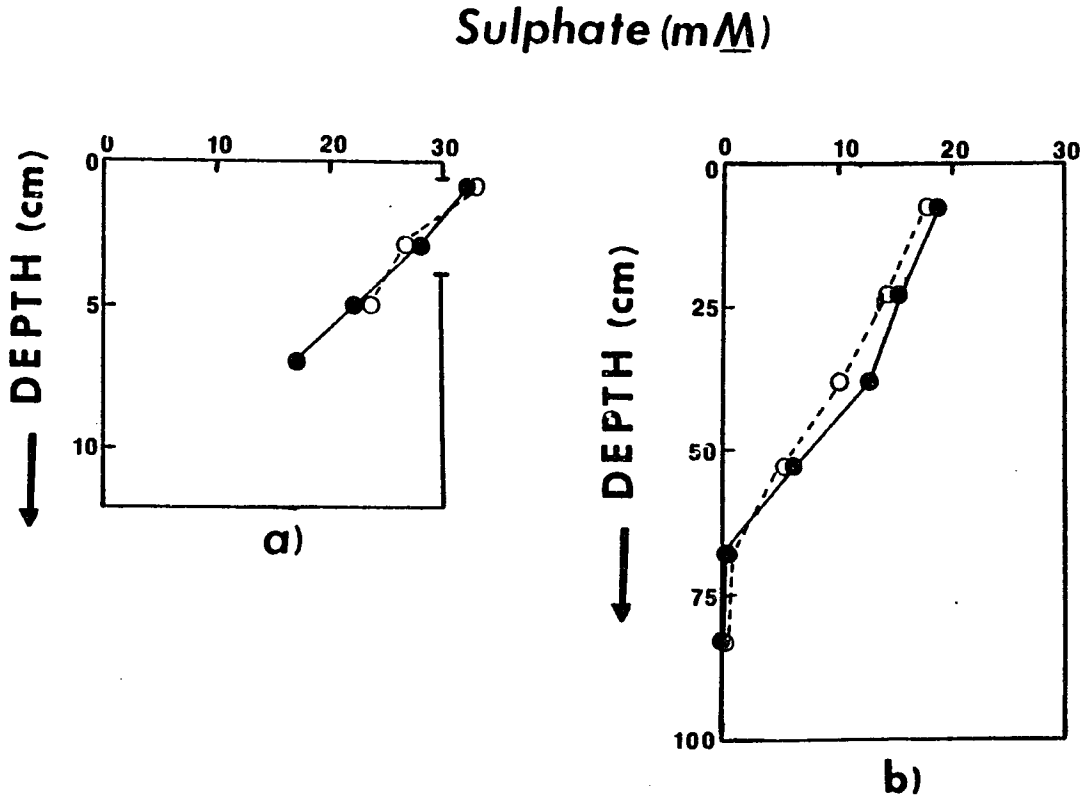

Figure 3-5. Sulphate concentrations (mM), versus depth (cm), for oxic (o---o), and anoxic subsamples (●—●): a) Core OAX-B, Site 3 (6-12-80); and b) Core OAX-I, Site 4 (10-21-80).

dation in aquatic systems have shown this reaction to be sluggish and very complex (Cline and Richards, 1969; Chen and Morris, 1972; and Almgren and Hagstrom, 1974). In addition, endproducts other than sulphate have been observed to be produced following sulphide oxidation; including sulphite and thiosulphate (Cline and Richards, 1969).

Total Iron. Previous workers have observed decreases in the concentration of total iron in anoxic pore water as a result of exposure to atmospheric oxygen (Troup et al., 1974; Loder et al., 1978; and Lyons et al., 1979d). Losses of total iron up to nearly 80% were observed in these studies. A similar effect was observed in this work at total dissolved iron levels of greater than 1 ppm. These results for two cores from Great Bay are presented in Table 3-4. As much as 89% of the total iron in samples of greater than 1 ppm, may be lost upon exposure to oxygen. As mentioned earlier, this loss is primarily the result of the formation of insoluble iron(III) oxi-hydroxides in the pore water (Troup et al., 1974). This reaction proceeds rapidly at the pH of pore water (Stumm and Morgan, 1970). At total dissolved iron levels of less than about 1 ppm in these cores, oxidation of the sediment samples actually resulted in net increases in the pore water iron concentrations. This effect may be a result of the oxidation of authigenic iron minerals and/or iron bound to organic matter in the sediments, resulting in the input of iron to the pore water. Alternatively, this effect may simply be due to lateral variability at these low iron levels. The anomalous anoxic and oxic iron values in the 30-45 cm section of core OAX-III (Table 3-4), may have been the result of a labelling error.

A significant question concerning these results is why does

Table 3-4. Effects of oxidation on total iron concentrations in anoxic pore water.

Core OAX-B
Date; 6-12-80
Site 3 (Adams Cove)

Depth (cm)	Total Iron Anoxic (ppm)	Total Iron Oxic (ppm)
0-3	2.13	0.66
3-6	0.54	0.52
6-9	0.16	0.37
9-12	0.12	0.25
12-15	0.12	0.23

Core OAX-III
Date: 4-15-81
Site 4 (Footman Islands)

Depth (cm)	Total Iron Anoxic (ppm)	Total Iron Oxic (ppm)
0-15	6.81	0.72
15-30	4.50	0.54
30-45	1.13	2.33
45-60	6.94	3.41
60-75	6.18	1.06

any measurable iron remain in the pore water following oxidation? As illustrated in core OAX-B (Table 3-4), there appears to be a certain threshold level of iron, below which even long oxygen exposure times (e.g. 1½ hours in this study), fail to remove all of the iron from the solution. This same critical iron level has been observed by Lyons et al., (1979d), and was attributed by these workers to organically associated iron. Presumably, the organic matter will either prevent oxidation of the bound Fe^{2+} (or at least kinetically hinder this process), or formation of insoluble Fe^{3+} species. Figure 3-6 presents the data in Table 3-4 graphically, and also a plot of total iron concentrations to values of oxidative iron loss. A strong linear correlation is evident, with oxidative iron loss proportional to the concentration of total iron in the unoxidized pore water. This is consistent with the idea that oxidation of Fe^{2+} to Fe^{3+}, and removal of iron oxi-hydroxides from solution is fact and nearly complete. Inclusions of all points from Table 3-4 in the correlation resulted in the theoretical line presented in Figure 3-6b ($r^2 = 0.876$). The value of the X intercept in this curve (about 0.6 ppm total iron), may represent the quantities of organically associated iron in the pore water of these cores.

The results of a brief study to assess the effects of oxidation on the molecular size distribution of total iron in anoxic pore water are presented in Table 3-5. These data indicate that a large fraction of the total iron in oxidized subsamples is able to pass a 50,000 nominal molecular weight cutoff filter than is true for subsamples processed anoxically. This was a surprising result since it was expected that the formation of iron(III) oxi-hydroxides following oxidation of dissolved Fe^{2+} would prevent passage of any iron in the oxidized samples through the filter. Even in pore water samples processed

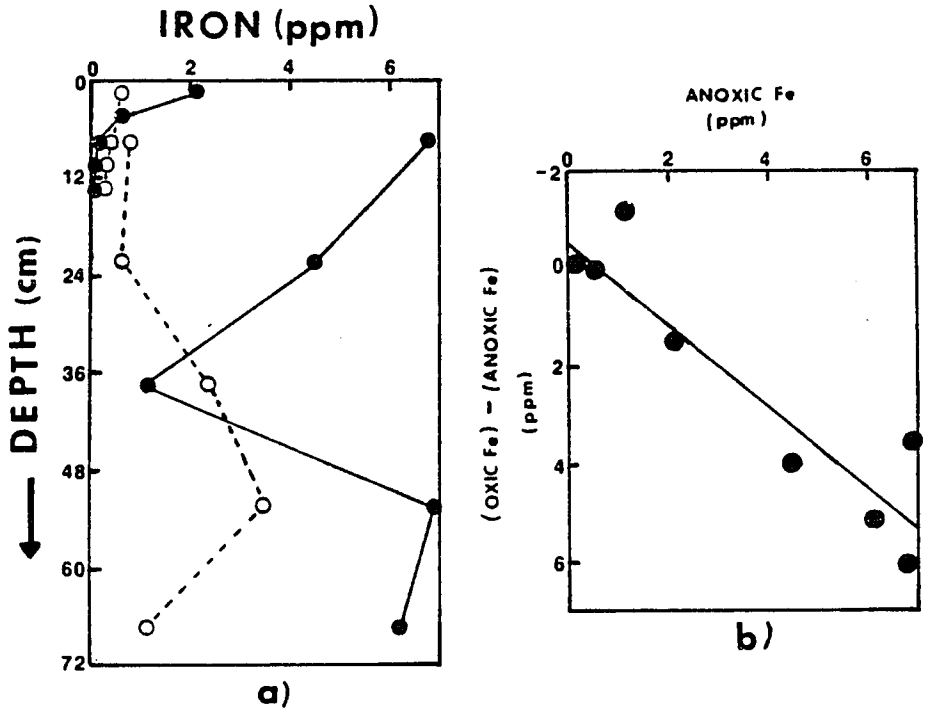

Figure 3-6. Effects of oxidation on the concentration of total iron (ppm) in anoxic pore water: a) Total Fe (ppm), versus depth (cm), for a box core (Core OAX-B, Site 3 (6-12-80)), and a gravity core (Core OAX-III, Site 4 (4-15-81)), with anoxic (●——●), and oxic subsamples; and b) a plot of total anoxic Fe (ppm), versus oxidative iron loss (ppm), for these same two cores (see text for discussion).

Table 3-5. Effects of oxidation on the molecular size distribution of iron in anoxic pore water.

Core OAX-B
Date: 6-12-80
Site 3 (Adams Cove)

Anoxic Subsample

Depth (cm)	Total Fe (ppm)	Fe <50,000 MW Range[a] (ppm)	Fe <50,000 MW Range[a] (%)
0-3	2.13	0.07	3.3
3-6	0.54	0.08	15
6-9	0.16	0.07	44
9-12	0.12	0.02	17

Oxic Subsample

Depth (cm)	Total Fe (ppm)	Fe <50,000 MW Range[a] (ppm)	Fe <50,000 MW Range[a] (%)
0-3	0.66	0.25	38
3-6	0.52	0.23	44
6-9	0.37	-	-
9-12	0.25	0.08	32

a) Separation achieved using Amicon XM-50 ultrafiltration membranes (50,000 nominal molecular weight cutoff).

anoxically, a very large percentage of the total iron (often as high as 90%; see discussion in Chapter 4), fails to pass a 50,000 MW nominal cut-off filter. One possible explanation for this effect may be the production of low molecular weight iron (e.g. <50,000 MW), by the oxidation of iron sulphide minerals or organically bound iron in the sediments. Alternatively, organically bound iron in the pore water of high molecular weight (e.g. >50,000 MW), may be cleaved by an oxidative process to produce lower molecular weight material. Implicit in any of these mechanisms, however, is the necessity of preventing the low molecular weight iron produced from forming iron(III) oxi-hydroxide colloids. The observation that actual enrichment of iron in the oxic subsamples was generally observed at very low iron concentrations (e.g. <1 ppm, see Table 3-4), tends to support the hypothesis that some iron may 'dissolve' in the pore water from the sediments during oxidation. However, these speculations are based on limited data, and further work is needed to substantiate these findings.

Nutrients. The effect of oxygen exposure on the concentrations of PO_4^{3-}, NH_{4+} and SiO_4^{4-} in anoxic pore water from Great Bay sediments was also investigated. The results of these experiments for PO_4^{3-} are presented in Table 3-6 and illustrated in Figure 3-7. Large PO_4^{3-} decreases in the oxidized subsamples were observed in all four cores. The overall average PO_4^{3-} loss following oxidation for all four cores was 40%, however, these decreases ranged from 4.5% up to 94%. The range and average percentage PO_4^{3-} losses for each core are summarized in Table 3-7. Loder et al., (1978), observed PO_4^{3-} losses of 14% to 71% in oxidized pore water from Great Bay, N.H. sediments. As mentioned earlier these PO_4^{3-} losses are thought to be a consequence of co-precipitation

Table 3-6. Effects of oxidation on PO_4^{3-} concentrations (μM), in anoxic pore water.

Core OAX-A
Date: 7-23-79
Site 4 (Footman Islands)

Depth (cm)	Anoxic PO_4^{3-} (μM)	Oxic PO_4^{3-} (μM)
0-2	17.0	5.17
2-4	45.5	5.17
4-6	57.0	3.40
6-8	56.2	10.0
8-10	86.5	13.1
10-12	91.0	14.1

Core OAX-B
Date: 6-12-80
Site 3 (Adams Cove)

Depth (cm)	Anoxic PO_4^{3-} (μM)	Oxic PO_4^{3-} (μM)
0-3	41.5	24.0
3-6	121	103
6-9	151	115
9-12	168	97.7
12-15	159	113

Core OAX-I
Date: 6-23-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic PO_4^{3-} (μM)	Oxic PO_4^{3-} (μM)
0-15	27.7	
15-30	86.5	68.5
30-45	132	111
45-60	106	98.8
60-75	105	84.5
75-90	112	104

Core OAX-II
Date: 10-21-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic PO_4^{3-} (μM)	Oxic PO_4^{3-} (μM)
0-15	30.9	24.1
15-30	-	31.5
30-45	95.2	90.9
45-60	110	59.4
60-75	116	108

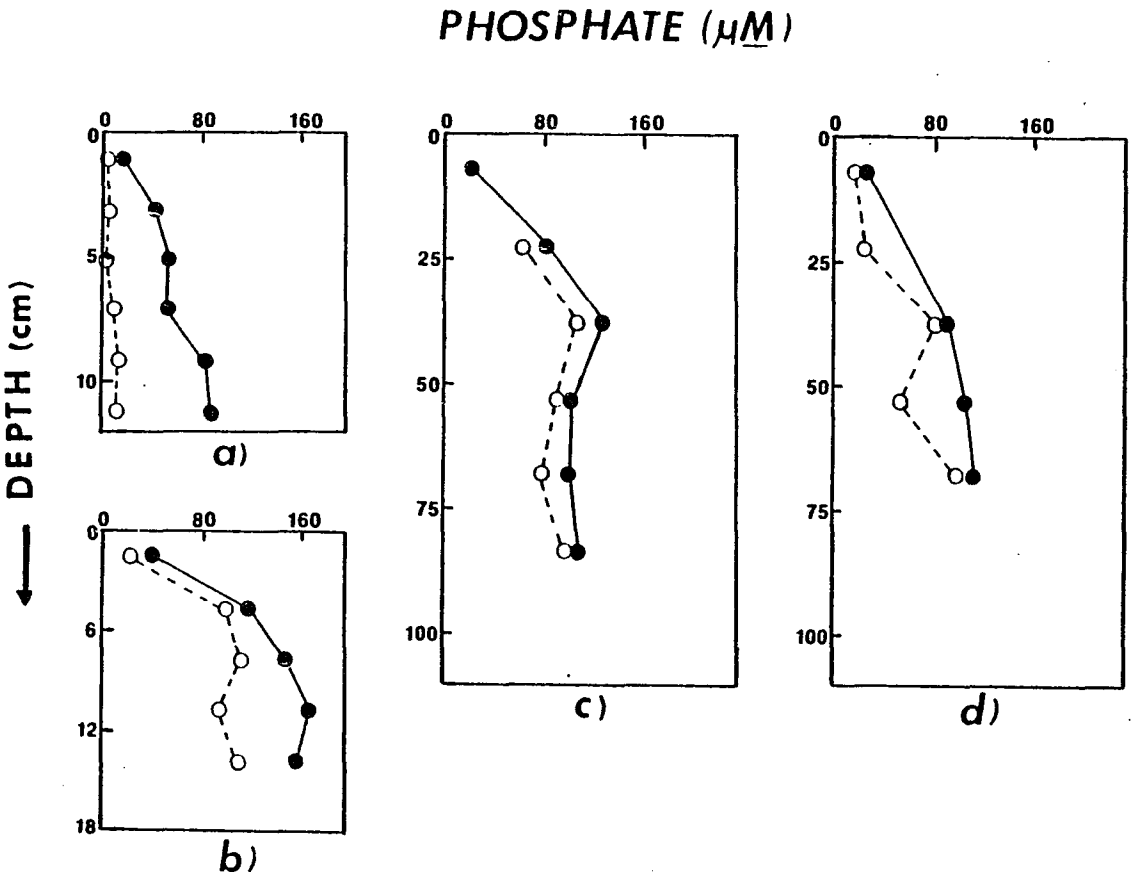

Figure 3-7. Phosphate concentrations (μM), versus depth (cm), for the cores from Table 3-6: a) Core OAX-A, Site 4 (7-23-79); b) Core OAX-B, Site 3 (6-12-80); and c) Core OAX-I, Site 4 (6-23-80); and d) Core OAX-II, Site 4 (10-21-80). For each core, pore water processed under anoxic (●—●), and under oxic (o---o), conditions are plotted side by side.

Table 3-7. Percentage of PO_4^{3-} losses compared to total iron concentrations for the four cores from Table 3-6.

Core	No. of Samples	PO_4^{3-} Loss (%) Average	PO_4^{3-} Loss (%) Range	Total Fe (μM) Average	Total Fe (μM) Range
OAX-A	6	84.0	(69.6-94.0)	-	
OAX-B	5	30.3	(14.9-42.2)	10.7	(1.8-38.1)
OAX-I	5	14.0	(6.8-20.8)	3.6	(1.8- 5.4)
OAX-II	4	19.9	(4.5-46.0)	43.0	(16.1-80.6)

of PO_4^{3-} on iron(III) oxi-hydroxide colloids which are formed following oxidation of Fe^{2+} in the pore water (Bray et al., 1973); Loder et al., 1978; and Lyons et al., 1979d). However, in core OAX-B large PO_4^{3-} decreases were observed even in core sections showing net increases of total iron in the oxidized subsamples (see Table 3-4 and 3-6). In addition, no significant correlation between total iron concentration and percentage PO_4^{3-} loss was observed (Table 3-7), even though it was shown earlier that the concentration of total iron is directly related to the amount of oxidative iron loss. These results do not imply that scavanging of PO_4^{3-} from pore water by iron(III) oxi-hydroxides following oxidation is an unimportant process. However, it appears that other mechanisms are also involved in the removal of PO_4^{3-} from pore water following oxidation.

Losses of ammonia from oxidized pore water samples (relative to samples processed anoxically), were also observed. However, percentage ammonia decreases were considerably lower than those observed for PO_4^{3-}. The results from this study for ammonia are presented in Table 3-8 and Figure 3-8. The average ammonia loss for the three cores in Table 3-8 was 8.9%; however, for a number of core sections no significant ammonia loss was observed, and in at least two sections from core OAX-I a net increase of ammonia in the pore water was observed. These ammonia losses are unlikely to have been a result of co-precipitation with iron(III) oxi-hydroxides after oxidation; since no correlation between iron and ammonia losses in core OAX-B was observed. Degassing of ammonia from pore water as NH_3 is also unlikely to have had the observed effect, since at the pH of interstitial water (7 to 8), less than 3% of the total ammonia is present as NH_3 (Gieskes and Rogers, 1973), and samples were acidified to pH less than 4 for storage. Oxidation

Table 3-8. Effects of oxidation on NH_4^+ concentrations (μM), in anoxic pore water.

Core OAX-B
Date: 6-12-80
Site 3 (Adams Cove)

Depth (cm)	Anoxic NH_4^+ (μM)	Oxic NH_4^+ (μM)
0-3	265	267
3-6	419	425
6-9	570	559
9-12	678	593
12-15	623	577

Core OAX-I
Date: 6-23-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic NH_4^+ (μM)	Oxic NH_4^+ (μM)
0-15	45.4	13.1
15-30	263	269
30-45	561	484
45-60	517	564
60-75	577	609
75-90	702	677

Core OAX-II
Date: 10-21-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic NH_4^+ (μM)	Oxic NH_4^+ (μM)
0-15	100	94.6
15-30	-	249
30-45	491	419
45-60	604	461
60-75	689	702

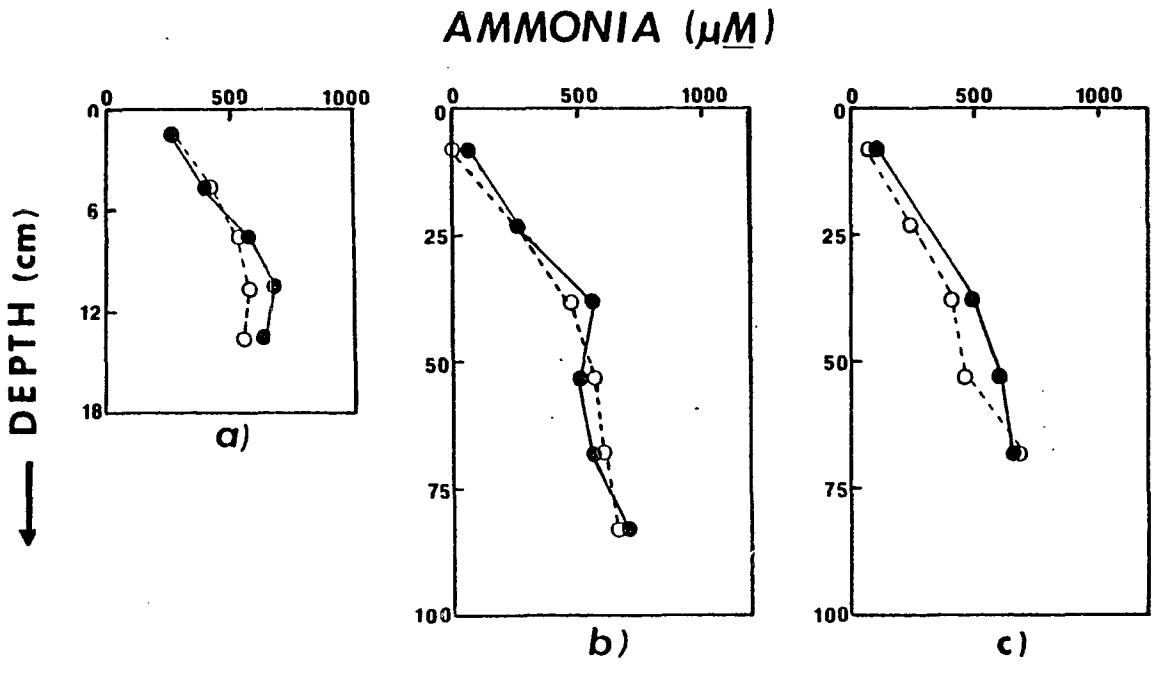

Figure 3-8. Ammonia concentrations (μM), versus depth (CM), for the cores from Table 3-8: a) Core OAX-B, Site 3 (6-12-80); b) Core OAX-I, Site 4 (6-23-80); and c) Core OAX-II, Site 4 (10-21-80). For each core, pore water processed under anoxic (●——●), and under oxic (o---o), conditions are plotted side by side.

of ammonia to nitrate in marine sediments may occur by biochemical nitrification (Barnes et al., 1975; Bender et al., 1977; and Grundmanis and Murray, 1977). However, even under conditions of high oxygen content, nitrification rates in the sediments are too low to account for the observed ammonia losses in some core sections during the 1½ hour processing period (Reddy and Patrick, 1976; Billen, 1978; and Henriksen et al., 1981). In addition, the pH of the samples during storage (e.g. <pH 4), was too low to allow for active nitrification (Focht and Verstraete, 1977). A purely chemical oxidation of ammonia to nitrate has been observed in soils (Keeney, 1973), and the rate of this reaction increases with decreasing pH (Bremner and Fuhr, 1966; and Stevenson et al., 1970). It is possible that this reaction also occurs in marine pore water, particularly during storage at low pH. The anomalously high nitrate concentrations observed in many of the cores from Great Bay sediments (see discussion in Chapter 4), would tend to support this mechanism for ammonia loss. Finally, increased adsorption of ammonia on sedimentary organic matter in the oxidized subsamples could also account for the observed ammonia losses. Rosenfeld (1979), has shown that ammonia in anoxic pore water is readily adsorbed onto sedimentary organic matter. Changes in the polarity or structure of sedimentary organic matter as a result of exposure to oxygen (Templeton, 1980), might result in increased ammonia adsorption, and subsequent losses in the pore water.

The results of these oxidation experiments on SiO_4^{4-} concentrations in pore water are presented in Table 3-9, and illustrated in Figure 3-9. No significant, systematic effect was observed upon exposure of these cores to atmospheric oxygen. This result was surprising,

Table 3-9. Effects of oxidation of SiO_4^{4-} concentrations (μM), in anoxic pore water.

Core OAX-B
Date: 6-12-80
Site 3 (Adams Cove)

Depth (cm)	Anoxic SiO_4^{4-} (μM)	Oxic SiO_4^{4-} (μM)
0-3	391	433
3-6	393	409
6-9	407	399
9-12	395	334
12-15	447	359

Core OAX-I
Date: 6-23-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic SiO_4^{4-} (μM)	Oxic Sio_4^{4-} (μM)
0-15	83.8	64.2
15-30	80.0	67.5
30-45	93.4	85.3
45-60	68.0	103
60-75	56.3	49.1
75-90	66.6	66.1

Core OAX-II
Date: 10-21-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic SiO_4^{4-} (μM)	Oxic SiO_4^{4-} (μM)
0-15	95.8	93.9
15-30	-	60.3
30-45	69.0	68.0
45-60	93.9	36.6
60-75	63.2	81.0

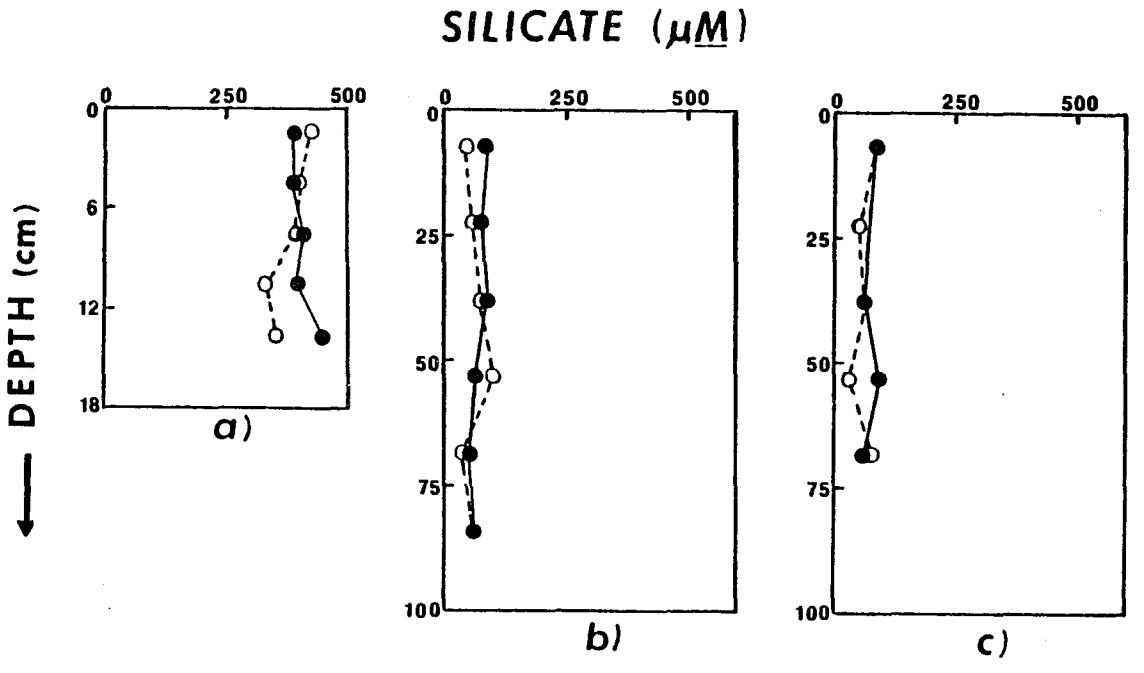

Figure 3-9. Silicate concentrations (μM), versus depth (cm), for the cores from Table 3-9: a) Core OAX-B, Site 3 (6-12-80); b) Core OAX-I, Site 4 (6-23-80); and c) Core OAX-II, Site 4 (10-21-80). For each core pore water processed under anoxic (●—●), and under oxic (o---o), conditions are plotted side by side.

since previous workers had observed silicate depletion in the pore water following exposure to oxygen (Loder et al., 1978; and Lyons et al., 1979d). Silicate losses following oxidation have been attributed to co-precipitation of the SiO_4^{4-} with iron(III) oxi-hydroxides (Lal et al., 1964; Loder et al., 1978; and Lyons et al., 1979d), or hydrated oxides of iron (Kato, 1969). Loder et al. (1978), observed considerably higher iron concentrations in their cores than were observed in the cores from this study (see Table 3-7); and it may be that insufficient iron was available in the cores from this work to observe a silicate oxidation effect. However, Lyons et al. (1979d), observed depletion of silicate in carbonate sediments even under conditions of zero iron loss. Thus, it appears that losses of silicate following oxygen exposure are dependent on factors other than simply scavanging by insoluble iron species. For example, Templeton (1980), has observed polarity changes in water extracted sedimentary organic matter from Great Bay (e.g. increases in functionality of the organic matter), after exposure to atmospheric oxygen. This process may induce increased adsorption of silicate by the organic matter. This same process may also result in losses of ammonia and phosphate from the pore water, as alluded to above.

B. Effects of Oxidation on Dissolved Organic Matter

Concentration of DOC. The effects of oxygen exposure on the concentration of DOC in the top 12 cm of sediment from two Great Bay sites are presented in Table 3-10. Similar results for the three gravity cores from Site 4 are presented in Table 3-11. As discussed earlier, it was expected that the oxidation of Fe^{2+} in the pore water with the subsequent formation of insoluble iron(III) oxi-hydroxides would result

Table 3-10. Effects of oxidation on the concentration of DOC in the top 12 cm of Great Bay anoxic sediments.

Core OAX-A
Date: 7-23-79
Site 4 (Footman Islands)

Depth (cm)	Anoxic DOC (mgC/l)	Oxic DOC (mgC/l)	Δ^1 DOC (mgC/l)
0-2	224.1	114.2	-109.9
2-4	143.0	120.0	- 23.0
4-6	117.5	77.0	- 40.5
6-8	126.4	78.5	- 47.9
8-10	138.1	46.7	- 91.4
10-12	53.5	32.0	- 21.5

Core OAX-B
Date: 6-12-80
Site 3 (Adams Cove)

Depth (cm)	Anoxic DOC (mgC/l)	Oxic DOC (mgC/l)	Δ^1 DOC (mgC/l)
0-3	10.2	9.0	-1.2
3-6	13.5	13.6	+0.1
6-9	15.6	14.9	-0.7
9-12	17.9	16.3	-1.6
12-15	20.0	19.3	-0.7

1) Δ DOC = (Oxic DOC) - (Anoxic DOC)

Table 3-11. Effects of oxidation on DOC concentrations in gravity cores from Great Bay anoxic sediments.

Core OAX-I
Date: 6-23-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic DOC (mgC/l)	Oxic DOC (mgC/l)	Δ^a DOC (mgC/l)
0-15	14.3	11.5	-2.8
15-30	29.1	36.5	+7.4
30-45	46.5	43.2	-3.3
45-60	46.7	42.6	-4.1
60-75	46.1	44.1	-2.0
75-90	50.1	52.3	+2.2

Core OAX-II
Date: 10-21-80
Site 4 (Footman Islands)

Depth (cm)	Anoxic DOC (mgC/l)	Oxic DOC (mgC/l)	Δ^a DOC (mgC/l)
0-15	19.5	17.5	- 2.0
15-30	22.1	33.6	+11.5
30-45	33.4	40.1	+ 6.7
45-60	42.1	44.1	+ 2.0
60-75	43.3	62.2	+18.9

Core OAX-III
Date: 4-15-81
Site 4 (Footman Islands)

Depth (cm)	Anoxic DOC (mgC/l)	Oxic DOC (mgC/l)	Δ^a DOC (mgC/l)
0-15	16.8	16.9	+0.1
15-30	34.9	43.5	+8.6
30-45	58.9	60.4	+1.5
45-60	70.1	66.0	-4.1
60-75	75.1	75.5	-0.2

a) Δ DOC = (Oxic DOC) - (Anoxic DOC).

in the scavanging of DOC from solution. In fact, such a loss of DOC was observed following oxidation of the pore water in core OAX-A (Table 3-10); with an average DOC decrease of about 41% for this core. In contrast, only a 7% average loss of DOC was observed in core OAX-B. The difference in DOC losses between these two cores may be related to differences in the concentrations of iron and dissolved organic matter in the pore water. Unfortunately, no iron data exists for core OAX-A: however, the concentrations of iron in core OAX-B are very low. It is interesting to note that in sections of core OAX-B exhibiting net increases of dissolved iron in the oxidized subsamples, losses of DOC up to 9% were still observed. This suggests that in addition to scavanging by iron(III) oxi-hydroxides, other processes may also result in DOC losses after oxidation.

Quite different effects were observed for the three gravity cores in Table 3-11. The only significant changes in DOC concentrations between oxic and anoxic subsamples below the top 15 cm sections in these cores were increases in the DOC concentrations of the oxic samples. This effect is particularly pronounced in core OAX-II. Based on carbon mass balance considerations, the increases of DOC in the pore water are most likely due to oxidation of sedimentary organic matter. Templeton (1980), has shown that exposure of predominantly sedimentary organic matter to atmospheric oxygen results in decreasing molecular weight and increasing polarity of this material. These are exactly the type of effects that would be likely to increase the solubility of sedimentary organic matter. For the three gravity cores in Table 3-11, an overall average gain of 11.6% for DOC in the pore water was observed below 15 cm. In the top 15 cm, an overall average decrease in DOC of

9.8% was observed. This decrease is probably a result of the same factors involved in the DOC losses observed in the box cores discussed above. The different oxidation effects on DOC observed above and below 15 cm depths is illustrated in Figure 3-10. It is interesting to note that the effect of oxidation changes at about the depth of bioturbation and other advective processes (e.g. about 15 cm (Aller, 1977; Lyons et al., 1979b; and Hines et al., 1981)). The sedimentary organic matter at shallow depths has been subject to frequent oxygen exposure as a result of natural advective processes (e.g. bioturbation and wave and tidal stirring), and, in addition, may be considerably less reduced by microbial activity than sedimentary organic matter at depth (Goldhaber and Kaplan, 1975). Thus, sedimentary organic compounds in the top 15 cm core sections would likely be little affected by exposure to atmospheric oxygen during processing. On the other hand, organic matter on sediments below 15 cm may be in a more reduced state and subject to structural changes upon exposure to oxygen, resulting in dissolution of some of this material.

DOC Molecular Weight. In addition to the work on oxidation effects on DOC concentration discussed above, ultrafiltration of both oxic and anoxic subsamples from several cores was also performed to assess the effects of oxidation on the molecular size distribution of DOC in anoxic pore water. Templeton (1980), observed a change in the molecular weight of water extracted sedimentary organic matter following oxygen exposure, and it was thought that a similar process might affect DOC. Ultrafiltration was carried out as described in Chapter 2, except that oxic subsamples were ultrafiltered in the laboratory atmosphere. Preliminary processing of anoxic and oxic subsamples was performed as

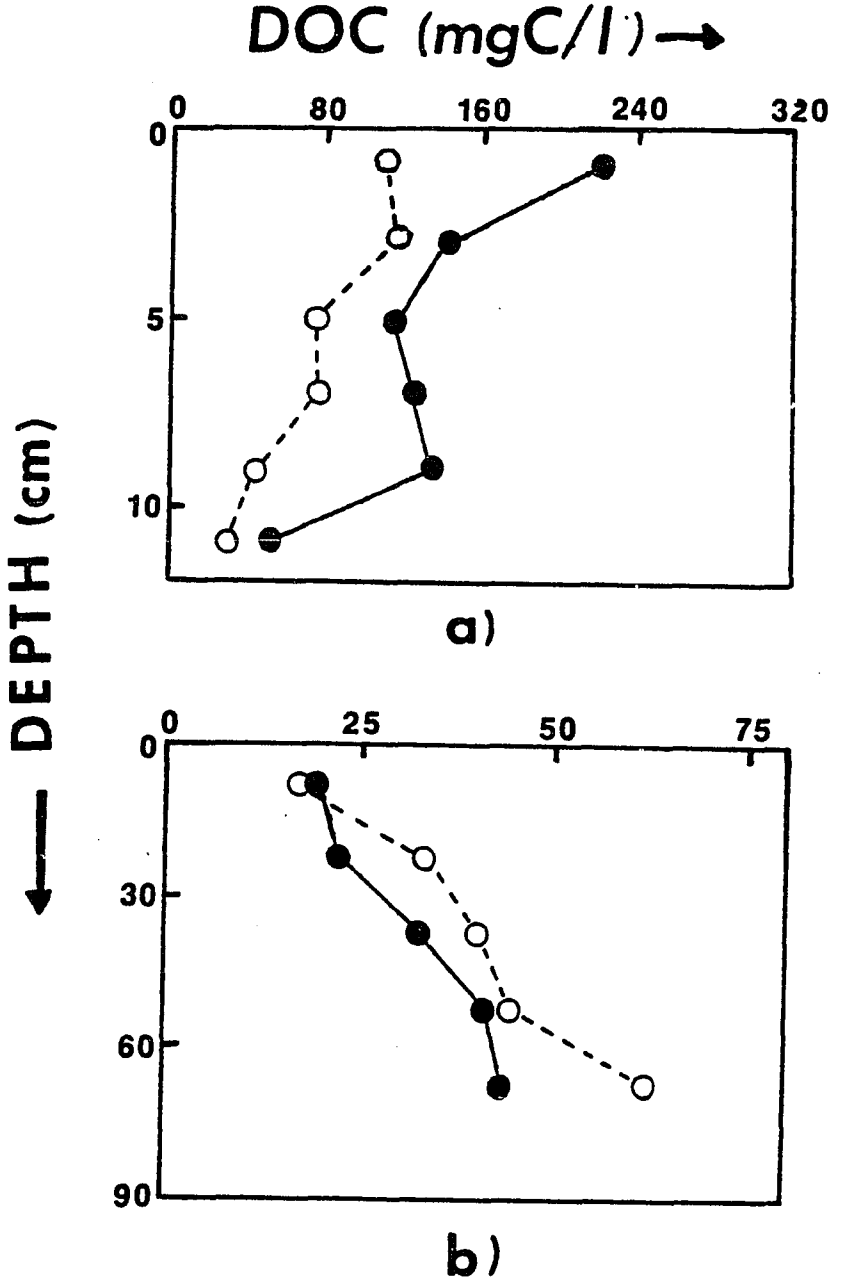

Figure 3-10. Comparison of DOC concentrations (mgC/l), in anoxic (●—●), and oxic (o---o), subsamples for a box core and a gravity core: a) Core OAX-A, Site 4 (7-23-79); and b) Core OAX-II, Site 4 (10-21-80).

described earlier. The results of these experiments are presented in Table 3-12. Molecular weight fractions of the DOC are presented both in mgC/l and as percentages of the total DOC as discussed in Chapter 2. These results are plotted in Figures 3-11 through 3-14.

In the two box cores (Figures 3-11 and 3-12), significant changes in the DOC molecular weight distribution following oxidation were observed. In the top 3 to 4 cm sections of both cores, significantly more low molecular weight DOC (e.g. less than 1,000 MW, and conversely, singificantly less DOC of molecular weight greater than 50,000 MW, was observed in the oxidized samples. Below this level, the opposite effect was evident in the oxic subsamples (e.g. a larger fraction of greater than 1,000 MW organic matter). In core OAX-A, these results could be accounted for by preferential loss of high molecular weight DOC at the surface and low molecular DOC below 4 cm. Alternatively, this effect could be a result of structural changes in the DOC left in solution following oxidation. However, in core OAX-B insufficient DOC is lost from the pore water after oxidation to account for the observed changes in the molecular weight distribution of the oxic subsample. Thus, at least in core OAX-B, oxidation is causing structural modification of the dissolved organic matter. In the top 4 cm, the effect of oxidation is the cleaving of large molecular weight DOC or possibly the breakup of inorganic/organic colloids to form low molecular weight DOC. It is interesting to note that the 2-4 cm zone is the region of change from oxic to anoxic conditions (from visual observation of the cores), in both box cores. Below this depth, oxidation of the pore water apparently results in some type of polymerization of the DOC, or formation of large molecular weight inorganic/

Table 3-12. Effects of oxidation on the molecular size distribution of dissolved organic carbon in anoxic pore water.

Core OAX-A
Date: 7-23-79
Site 4 (Footman Islands)

Anoxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-2	224.1	217.8	97.2	6.3	2.8
2-4	143.0	140.2	98.0	2.8	2.0
4-6	117.5	105.8	89.8	11.7	10.2
6-8	126.4	-	-	-	-
8-10	138.1	115.6	83.7	22.5	16.3
10-12	53.5	23.1	43.2	30.4	56.8

Oxic Subsample

Depth (cm)	Total DOC (mgC.l)	DOC > 1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-2	114.2	75.0	65.7	39.2	34.3
2-4	120.0	111.4	92.8	8.6	7.2
4-6	77.0	76.4	99.2	0.6	0.8
6-8	78.5	75.3	95.9	3.2	4.1
8-10	46.7	-	-	-	-
10-12	32.0	19.0	59.4	13.0	40.6

Table 3-12. continued.

Core OAX-B
Date: 6-12-80
Site 3 (Adams Cove)

Anoxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 50000 (mgC/l)	(%)	DOC 50000-1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-3	10.2	3.2	31.4	1.3	12.7	5.7	55.9
3-6	13.5	3.2	23.7	5.2	38.5	5.1	37.8
6-9	15.6	1.5	9.6	7.0	44.9	7.1	45.5
9-12	17.9	1.2	6.7	10.4	58.1	6.3	35.2
12-15	20.0	1.2	6.0	10.2	46.0	8.6	43.0

Oxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 50000 (mgC/l)	(%)	DOC 50000-1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-3	9.0	1.9	24.4	0.3	3.3	6.8	78.9
3-6	13.6	3.6	26.5	6.2	45.6	3.8	27.9
6-9	14.9	3.1	20.8	7.0	47.0	4.8	32.2
9-12	16.3	2.8	17.2	8.8	54.0	4.7	28.8
12-15	19.3	4.0	20.7	9.7	50.3	5.6	29.0

Table 3-12. continued.

Core OAX-I
Date: 6-23-80
Site 4 (Footman Islands)

Anoxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 50000 (mgC/l)	(%)	DOC 50000-1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-15	14.3	6.2	43.4	3.4	23.8	4.7	32.9
15-30	29.1	11.0	37.8	13.7	47.1	4.4	15.1
30-45	46.5	8.0	17.2	33.3	71.6	5.2	11.2
45-60	46.7	10.7	22.9	28.9	61.9	7.1	15.2
60-75	46.1	10.1	21.9	31.0	67.2	5.0	10.8
75-90	50.1	11.8	23.6	34.7	69.3	3.6	7.2

Oxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 50000 (mgC/l)	(%)	DOC 50000-1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-15	11.5	6.2	53.9	3.1	27.0	2.2	19.1
15-30	36.5	12.3	35.8	19.9	54.5	4.3	11.8
30-45	43.2	14.0	32.4	26.1	60.4	3.1	7.2
45-60	42.6	6.0	14.1	33.8	79.3	2.8	6.6
60-75	44.1	9.4	21.3	29.7	67.3	5.0	11.3
75-90	52.3	17.2	32.8	32.1	61.4	3.0	5.7

Table 3-12. continued.

Core OAX-III
Date: 4-15-81
Site 4 (Footman Islands)

Anoxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 50000 (mgC/l)	(%)	DOC 50000-1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-15	16.8	3.5	20.8	6.5	38.7	6.8	40.5
15-30	34.9	5.6	16.0	23.6	67.6	5.7	16.3
30-45	58.9	10.7	18.2	39.5	67.1	8.7	14.8
45-60	70.1	7.9	11.3	46.2	65.9	16.0	22.8
60-75	75.7	8.0	10.6	50.9	67.2	16.8	22.2

Oxic Subsample

Depth (cm)	Total DOC (mgC/l)	DOC > 50000 (mgC/l)	(%)	DOC 50000-1000 (mgC/l)	(%)	DOC < 1000 (mgC/l)	(%)
0-15	16.9	0.8	4.7	0	0	16.2	95.9
15-30	43.5	2.0	4.6	22.7	52.2	18.8	43.2
30-45	60.4	13.9	23.0	30.5	50.5	16.0	26.5
45-60	66.0	16.6	25.2	38.1	57.7	11.3	17.1
60-75	75.5	23.5	31.1	44.4	58.8	7.6	10.1

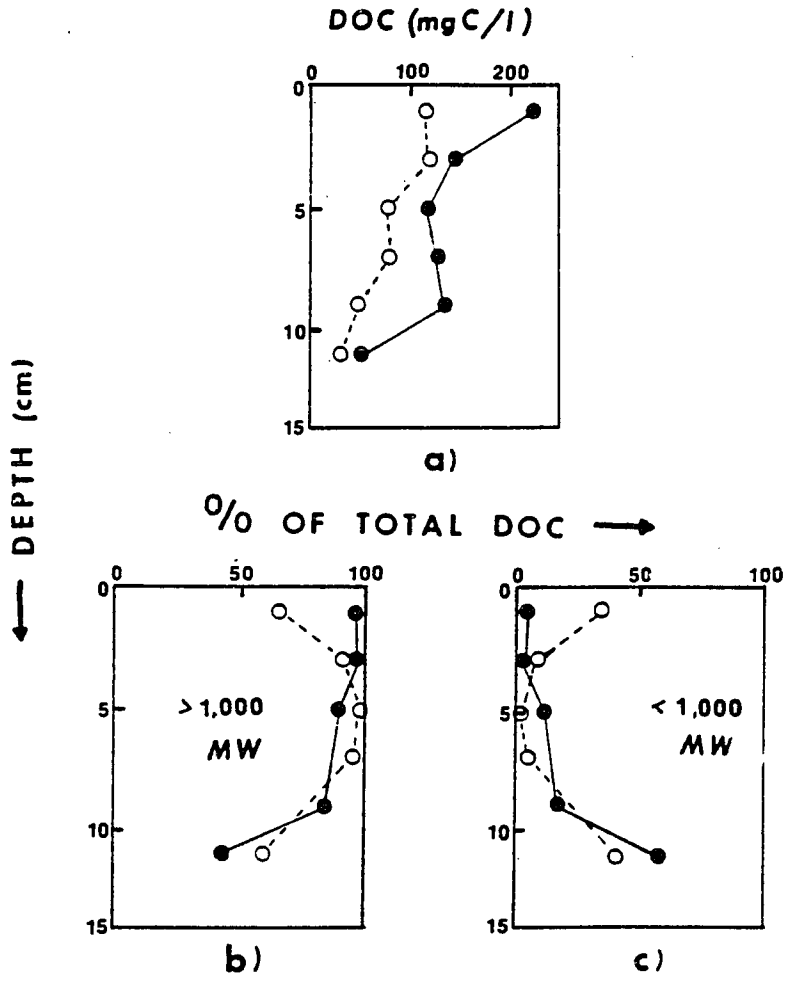

Figure 3-11. Comparison of DOC concentrations (mgC/l), and molecular size distribution for anoxic (●——●), and oxic (o---o), subsamples: Core OAX-A, Site 4 (7-23-79).

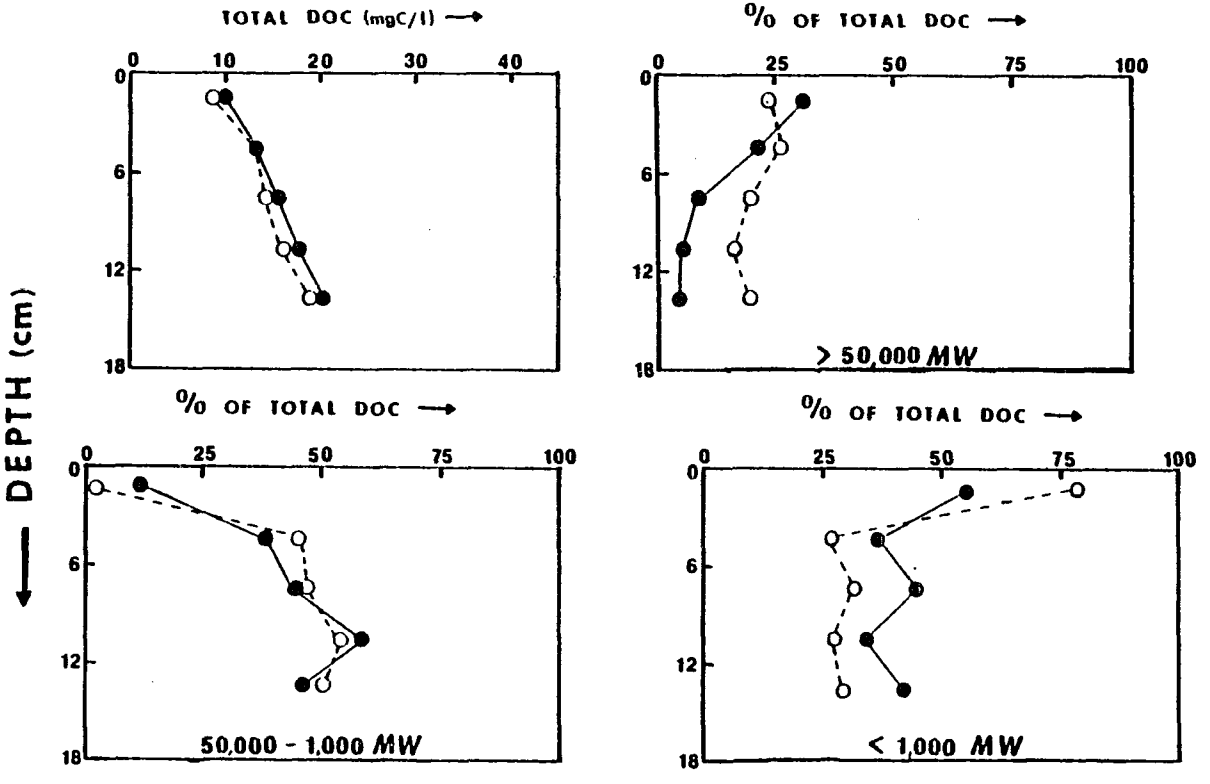

Figure 3-12. Comparison of DOC concentrations (mgC/l), and molecular size distributions for anoxic (●—●), and oxic (o---o), subsamples: Core OAX-B, Site 3 (6-12-80).

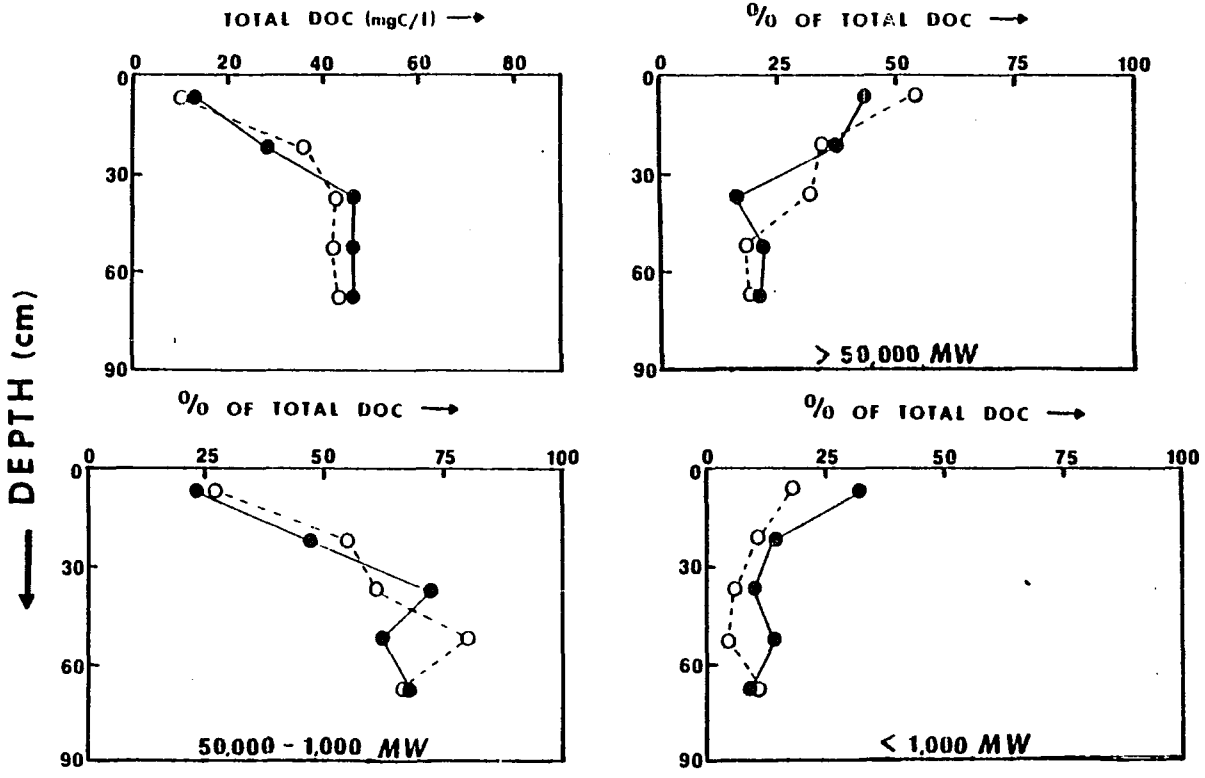

Figure 3-13. Comparison of DOC concentrations (mgC/l), and molecular size distributions for anoxic (●—●), and oxic (o---o), subsamples: Core OAX-I, Site 4 (6-23-80).

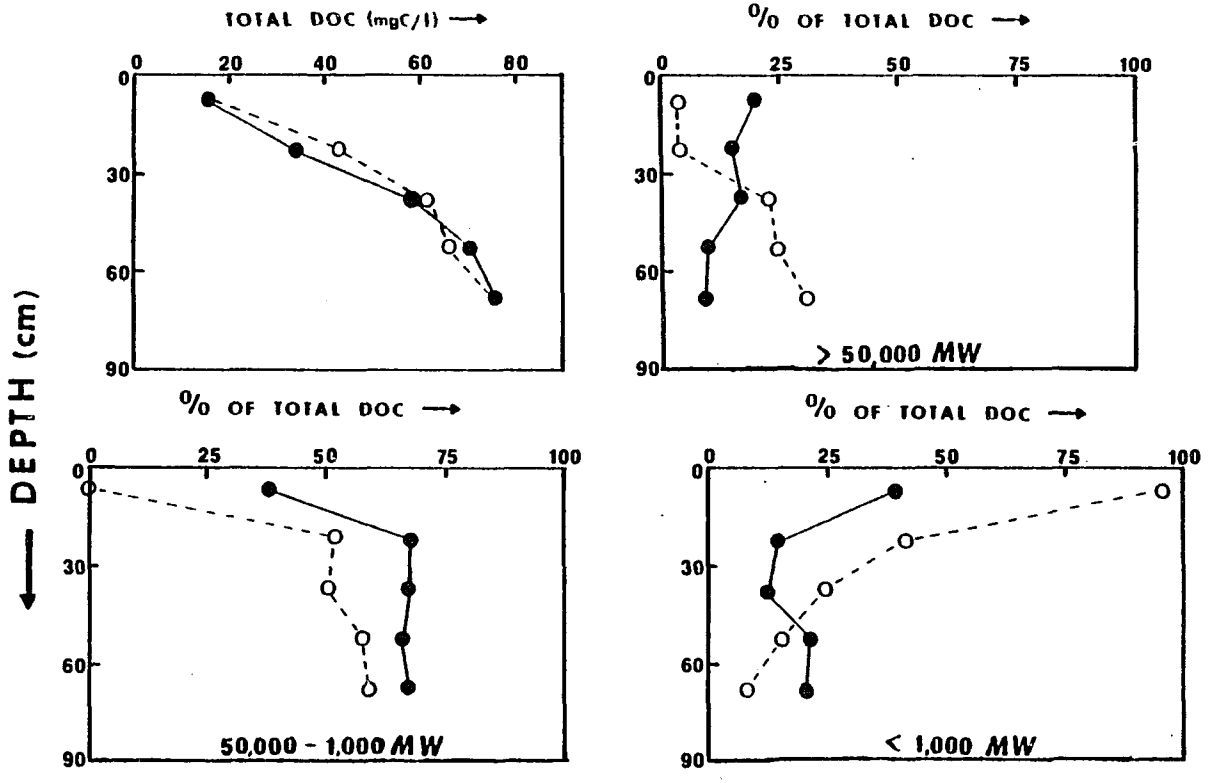

Figure 3-14. Comparison of DOC concentrations (mgC/l), and molecular size distributions for anoxic (●—●), and oxic (o---o), subsamples: Core OAX-III, Site 4 (4-15-81).

organic colloids. The mechanism involved in these transformations are unknown.

No significant effect on the molecular weight distribution of DOC in core OAX-I (Figure 3-13), was observed following oxidation. However, oxidation effects on the DOC molecular weight distribution of gravity core OAX-III were evident. As in box core OAX-B, little oxidation effect on the DOC concentrations in core OAX-III were observed. Thus, changes in the DOC molecular size distribution were due to structural changes instituted by reaction with molecular oxygen. In the top 45 cm, reaction with oxygen results in increased quantities of low molecular weight (less than 1,000), DOC in the pore water. Below this zone, DOC of molecular weight greater than 50,000 is produced as a result of reaction of DOC less than this molecular weight with oxygen. The increased percentage of low molecular weight DOC in the top 45 cm of the oxic subsamples could be a result of bacterial degradation of high molecular weight DOC during the processing period by facultative anaerobic bacteria switching over to aerobic respiration, with subsequent higher activities (Doelle, 1975). If this mechanism is indeed operating, it would be expected to decrease in importance with depth since bacterial populations have been observed to decrease with depth in sediment cores (Sorokin, 1962; and Hines, 1981). This is in accord with the observed effect. The increase in the percentage of high molecular weight DOC in oxidized subsamples below 45 cm may be a result of some type of polymerization reaction or the formation of inorganic/organic colloids.

Polarity of Dissolved Organic Matter. The effects of oxidation on the polarity of organic matter in anoxic pore water was investigated

using reversed phase HPLC. The conditions and methods used in the separation of dissolved organic matter by HPLC were discussed earlier (see Chapter 2). In this experiment, both oxic and anoxic subsamples from core OAX-II were analyzed using HPLC. The resulting chromatograms for the 0.15 cm section are illustrated in Figure 3-15. In the anoxic subsample from this core section, three fractions were exhibited in the liquid chromatogram. However, after oxidation the least polar fraction is considerably reduced in absorbance (254 nm). Similar results were obtained in all other core sections. The liquid chromatograms for the anoxic and oxic subsamples for the 45-60 cm core section are reproduced in Figures 3-16a and 3-16b, respectively. Again, three major fractions were present in the chromatogram of the anoxic subsample. In the oxic subsample of this core section, the least polar fraction is present only as a shoulder on the broad fraction. These results could be a result of decreased molecular weight and increased functionality of the dissolved organic matter following oxidation. A similar effect has been observed to occur as a result of oxidation of water extractable sedimentary organic matter from anoxic marine systems (Templeton, 1980).

III. Conclusions

The results of this study emphasize the necessity of maintaining oxygen-free conditions during all sample processing of anoxic marine pore water and sediments. Anoxic marine sediments exposed to atmospheric oxygen exhibited decreased concentrations of alkalinity, total iron, phosphate and ammonia in the pore water. The results for total iron and phosphate confirmed those obtained by previous workers (Bray et al., 1973; Troup et al., 1974; Loder et al., 1978; and Lyons et al., 1979d). However, loss of dissolved silicate from the pore water, which

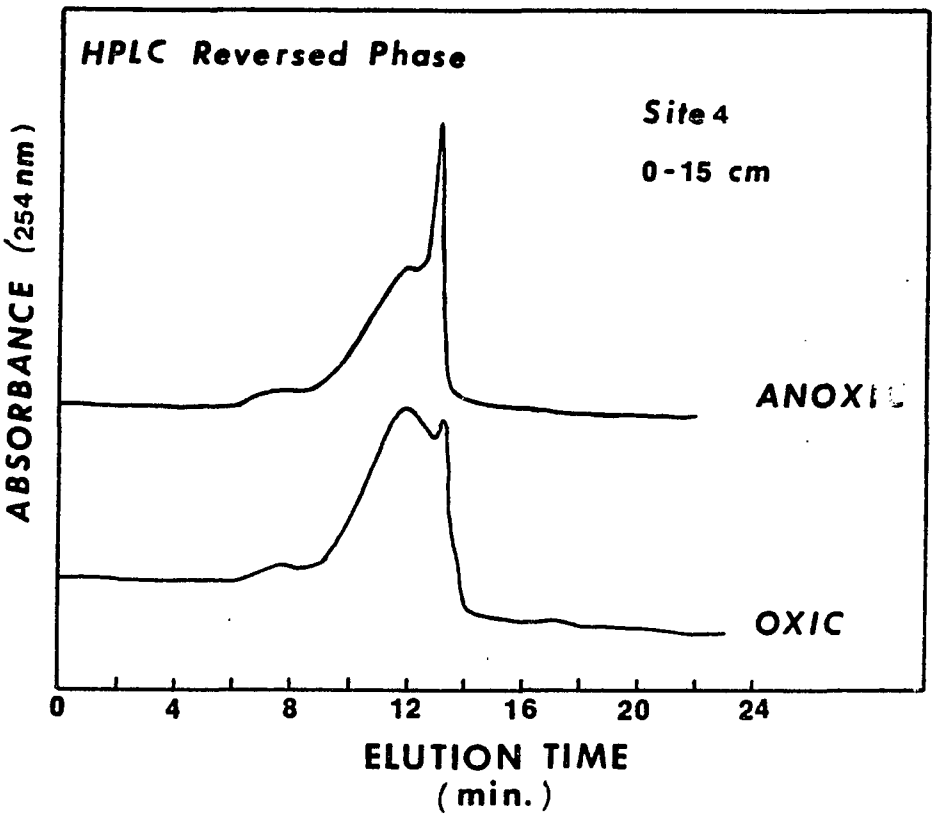

Figure 3-15. Effects of oxidation on the polarity of organic matter in anoxic pore water: Core OAX-II (0-15 cm section), Site 4 (10-21-80). The chromatogram labeled Anoxic had the sample processed under an N_2 atmosphere, while that labeled Oxic had the sample processed in the laboratory atmosphere.

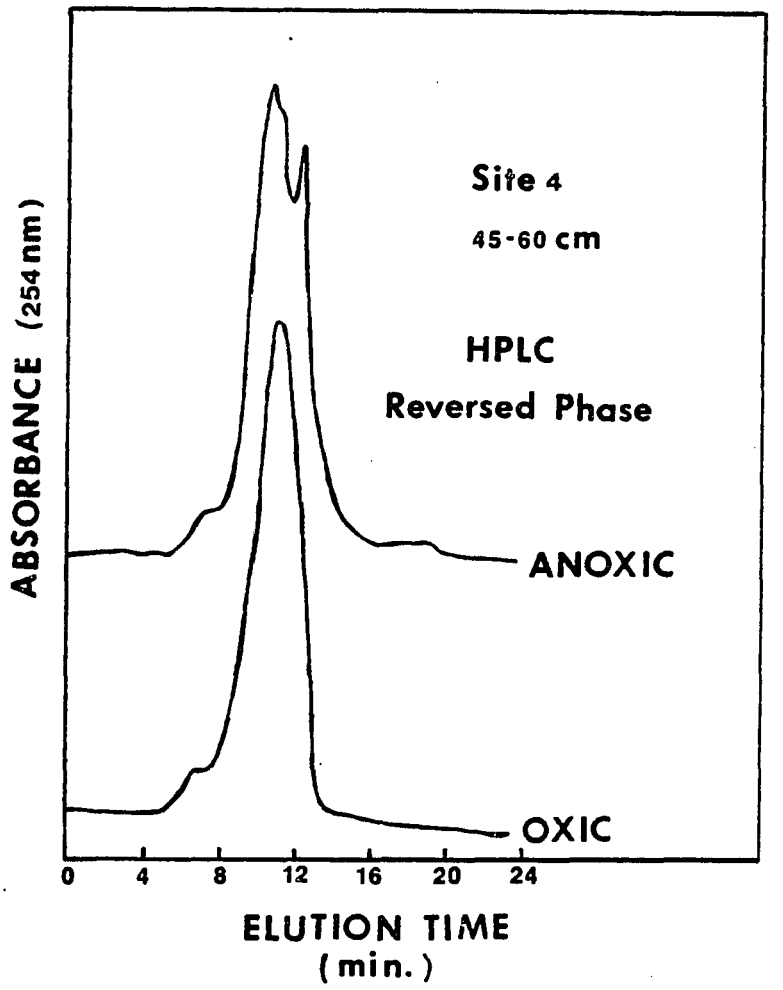

Figure 3-16. Effects of oxidation on the polarity of organic matter in anoxic pore water: Core OAX-II (45-60 cm section), Site 4 (10-21-80). The chromatogram labeled Anoxic had the sample processed under an N_2 atmosphere, while that labeled Oxic had the sample processed in the laboratory atmosphere.

had been observed by other researchers (Loder, et al., 1978; and Lyons et al., 1979d), was not consistently observed in this work (possibly due to differences in environmental factors). Decreased concentrations of DOC in the top 15 cm of sediment was observed following oxidation; probably as a result of co-precipitation with iron(III) oxi-hydroxides. However, in deeper core sections, net increases of DOC in the pore water of oxidized subsamples were observed. This unexpected result must be due to increasing solubility of sedimentary organic matter following reaction with atmospheric oxygen. In addition to these quantitative effects; the effects of reaction with oxygen on the structural integrity of dissolved organic matter formed under anoxic conditions were illustrated. Changes in both the molecular weight and polarity of dissolved organic matter following exposure to oxygen were observed. This emphasizes the necessity of not only processing anoxic pore water samples for structural analysis of dissolved organic matter under oxygen-free conditions, but also the need to store such samples under inert conditions.

Besides the sample processing and sample storage aspects of this work, some details of the nature of the organic matter in anoxic marine pore water were revealed. The observed increases in the concentration of DOC in pore water following exposure to oxygen, emphasizes the lability of the chemical bonds in sedimentary organic matter. This supports the conclusions of previous workers regarding the reactivity of reduced organic matter in the sediments (Hays et al., 1975; and Templeton, 1980). Templeton (1980), has suggested that these oxidation reactions may involve cleavage of amide or ester linkages; formed from condensation or polymerization reaction involving amino acids

and carbohydrates (Eglinton and Barnes, 1976; Young et al., 1977; and Carter and Metterer, 1978). In addition, the changes exhibited in the molecular weight distributions and reversed phase liquid chromatograms of DOC in anoxic pore water following oxidation indicate the similarity of much of this material to the sedimentary organic matter. It may be that the concept of totally separate pools of pore water and sedimentary organic matter is somewhat misleading. The evidence in this chapter and in Chapter 5 imply that a pool of organic matter exists in anoxic marine sediments, that is readily exchangable between the sediments and a 'dissolved' state; depending upon the conditions and possibly on the method of pore water extraction. Further work is needed to delineate these features more exactly.

CHAPTER 4

CHEMISTRY OF GREAT BAY ANOXIC SEDIMENTS AND PORE WATER

I. Introduction to Problem

In this chapter, data from the determination of chemical species or chemical characteristics in solid sediments and pore water from Great Bay, N.H. cores are presented. Solid sediment results presented include analyses for sediment size, organic carbon, nitrogen and phosphorus, and inorganic phosphorus. Pore water data presented here focus on inorganic species (e.g. pH, titration alkalinity, chloride, sulphate, nutrients and iron). Organic species in the pore water of Great Bay anoxic sediments are discussed in later chapters of this dissertation. The diverse suite of chemical data overviewed in this chapter will be used to develop an overall picture of the processes occurring during early diagenesis in Great Bay anoxic sediments. Many of the conclusions reached here will be drawn upon in later chapters, in the discussions of the diagenesis of organic matter.

Some earlier studies of Great Bay sediments for grain size (Haug, 1976; Armstrong et al., 1976 and Leavitt, 1980), and organic content (Lyons and Gaudette, 1979; and Leavitt, 1980), have been conducted. The results of these previous studies as they relate to the sediment analyses from this work are discussed below. Extensive work on the distribution of inorganic chemical species in anoxic pore water from nearshore marine sediments have been conducted in the past (Murthy

and Ferrell, 1972; Vanderborght and Billen, 1975; Manheim, 1976; Vanderborght et al., 1977a and 1977b; Martens et al., 1978; Murray et al., 1978; Rosenfeld, 1980; and Berner, 1980). A thorough discussion of these studies in terms of early diagenetic processes was presented earlier (see Chapter 1). In addition, some previous work on the distribution of inorganic species in pore water from Great Bay anoxic sediments has been conducted (Lyons et al., 1979b; Lyons and Gaudette, 1979; and Hines, 1981). These earlier studies are discussed in relation to the results from this work in the appropriate sections below.

There are two reasons for conducting studies of inorganic species in pore water in conjunction with studies of dissolved organic matter. First, many inorganic species in pore water are produced as byproducts of microbial degradation of organic matter (e.g. titration alkalinity, ammonia and phosphate (Berner, 1980)), and a number of other inorganic species (e.g. iron and silicate), may interact with dissolved organic matter in pore water (Lyons et al., 1979a; and Martens and Goldhaber, 1978). A second point is the necessity of making certain routine measurements when dealing with environmental samples to avoid incorrect interpretations of data in terms of the diagenetic reactions taking place. For example, chloride data from Site 3 (Adams Cove), indicated the presence of freshwater intrusion into the sediment from below. This information is essential for a correct interpretation of some anomalous DOC concentrations observed at this site.

All sampling, processing and analytical techniques used to obtain the results presented in this chapter, were outlined in Chapter 2. In order to make the text more readable, all numerical results are

tabulated in Appendixes A, B and C. Appendix A contains all of the solid sediment data. All of the results for dissolved inorganic species are presented in Appendix B (box cores), and C (gravity cores). The first sections of this chapter will concentrate on descriptive observations of the vertical, lateral and temporal variations of sediment characteristics and dissolved inorganic species. Later sections, however, will emphasize a more quantitative approach to early diagenesis, based on the use of kinetic models developed by Berner (1974, 1976 and 1980), and others (Vanderborght et al., 1977a and 1977b; Goldhaber et al., 1977; Aller, 1977; and Rosenfeld, 1977).

II. Results and Discussions

A. Solid Sediments

Sediment Size. Sediment samples from all five Great Bay sampling sites were separated into sand, silt and clay fractions, in order to determine the relative importance of each grain size at these locations. These results, plotted as functions of depth, are illustrated in Figure 4-1. The range, mean and standard deviation of the sediment data from each core are summarized in Table 4-1. The whole core average values as well as the surface sediment percentages of sand, silt and clay are presented on ternary diagrams in Figure 4-2.

No depth trends of grain size common to all five sampling locations were observed (Figure 4-1). This implies differences in the past depositional environments of the five sites. Site 1 in the Piscataqua River was observed to contain a high percentage of sand in the sediment, and increasing sand content with depth. The high sand content at this site is probably a consequence of the high tidal flow rate in the Piscataqua River. The fine grain fraction (e.g. silt +

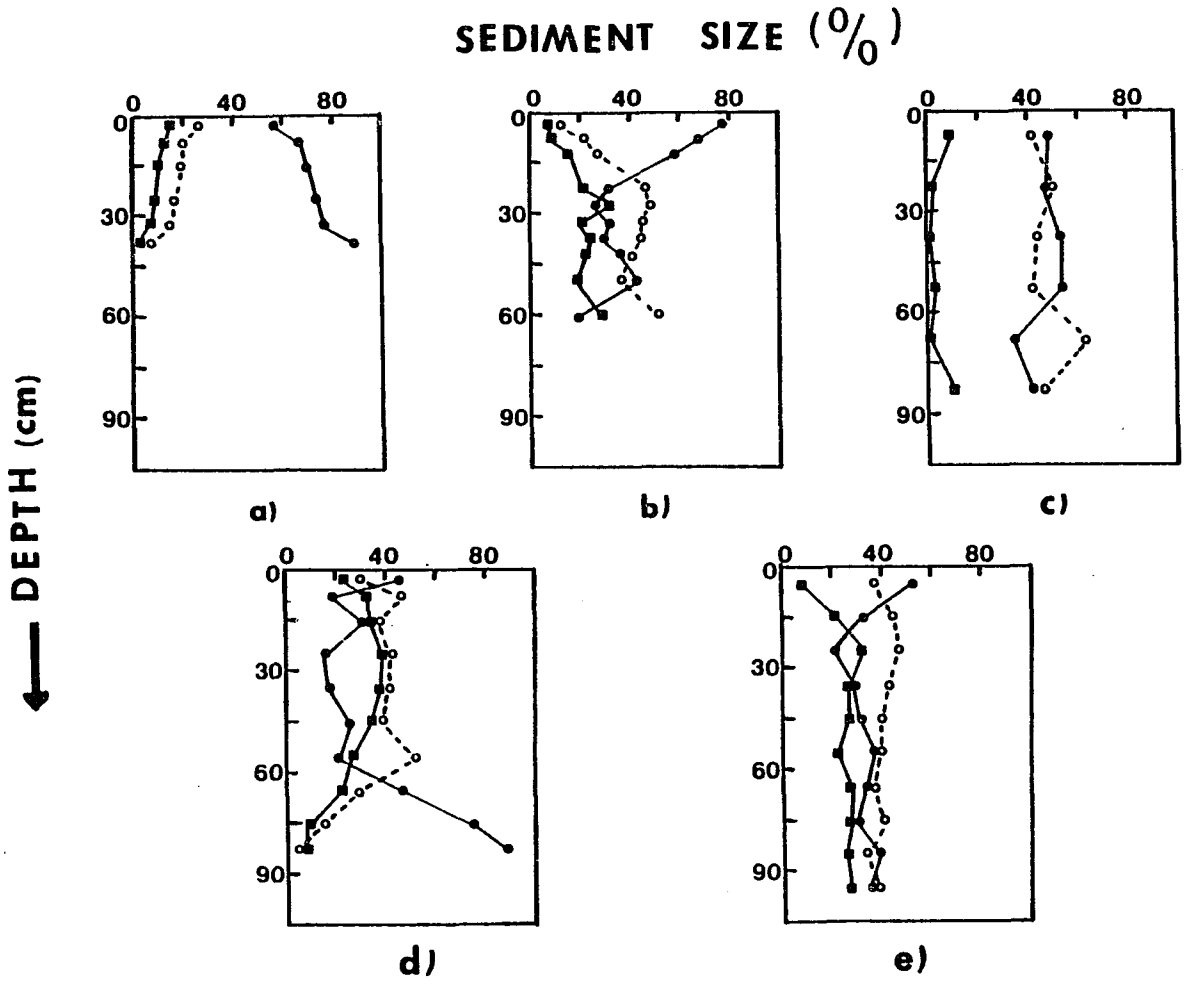

Figure 4-1. Percentages of sand (●—●), silt (o---o), and clay (■—■), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River).

Table 4-1. Summary of solid sediment results.

Site 1 (7-19-78)

	Range	Mean
% Sand	56.91 - 89.95	72.85
% Silt	6.979 - 27.55	17.59
% Clay	3.075 - 15.52	9.557
% OC[a]	0.76 - 1.51	1.16
% ON[b]	0.05 - 0.17	0.11
% OP[c]	0.0001 - 0.0192	0.0082
% IP[d]	0.0055 - 0.0211	0.0148
OC/ON	9.16 - 16.9	12.6
OC/OP	258 - 3310	1000
ON/OP	17.4 - 195	68.4
IP/OP	0.287 - 25.3	6.79

Site 2 (6-20-78)

	Range	Mean
% Sand	19.18 - 78.32	42.49
% Silt	12.88 - 51.76	37.59
% Clay	8.814 - 29.06	20.91
% OC[a]	1.60 - 0.73	1.21
% ON[b]	0.09 - 0.18	0.14
% OP[c]	0.0020 - 0.0130	0.0080
% IP[d]	0.0188 - 0.0260	0.0216
OC/ON	7.35 - 12.2	10.2
OC/OP	199 - 1480	501
ON/OP	19.8 - 202	54.1
IP/OP	1.45 - 11.7	3.70

a) OC = organic carbon

b) ON = organic nitrogen

c) OP = organic phosphorus

d) IP = Inorganic phosphorus

Table 4-1. continued.

Site 3 (7-11-80)

	Range	Mean
% Sand	34.97 - 54.27	41.27
% Silt	41.68 - 63.74	47.97
% Clay	1.291 - 11.14	4.762
% OC[a]	0.96 - 1.93	1.29
% ON[b]	0.09 - 0.18	0.13
% OP[c]	0.0001 - 0.0090	0.0062
% IP[d]	0.0408 - 0.0486	0.0464
OC/ON	11.2 - 13.2	11.9
OC/OP	440 - 1210	734
ON/OP	41.8 - 102	61.9
IP/OP	5.39 - 12.1	8.17

Site 4 (6-30-78)

	Range	Mean
% Sand	17.93 - 89.48	39.29
% Silt	5.152 - 51.77	33.61
% Clay	5.370 - 40.40	27.10
% OC[a]	0.65 - 3.46	2.25
% ON[b]	0.07 - 0.85	0.35
% OP[c]	0.0011 - 0.0147	0.0091
% IP[d]	0.0159 - 0.0256	0.0219
OC/ON	4.75 - 11.8	8.62
OC/OP	237 - 4020	1140
ON/OP	33.6 - 772	172
IP/OP	1.19 - 22.3	5.05

a) OC = organic carbon

b) ON = organic nitrogen

c) OP = organic phosphorus

d) IP = Inorganic phosphorus

Table 4-1. continued.

Site 4 (8-11-80)

	Range	Mean
% Sand	27.85 - 41.95	35.10
% Silt	47.26 - 67.06	53.40
% Clay	2.747 - 17.85	11.50
% OC[a]	2.20 - 3.87	3.20
% ON[b]	0.21 - 0.37	0.32
% OP[c]	0.0068 - 0.0124	0.0097
% IP[d]	0.0450 - 0.0574	0.0514
OC/ON	11.0 - 12.6	11.8
OC/OP	618 - 1350	916
ON/OP	55.3 - 107	77.1
IP/OP	3.63 - 7.82	5.85

Site 5 (8-10-78)

	Range	Mean
% Sand	20.57 - 53.53	34.67
% Silt	34.68 - 47.42	40.34
% Clay	8.321 - 32.01	24.98
% OC[a]	2.26 - 4.05	3.02
% ON[b]	0.25 - 0.33	0.29
% OP[c]	0.0062 - 0.0202	0.0141
% IP[d]	0.0126 - 0.0196	0.0157
OC/ON	9.07 - 14.9	12.0
OC/OP	324 - 1240	557
ON/OP	28.2 - 99.8	51.0
IP/OP	0.624 - 3.10	1.29

a) OC = organic carbon

b) ON = organic nitrogen

c) OP = organic phosphorus

d) IP = Inorganic phosphorus

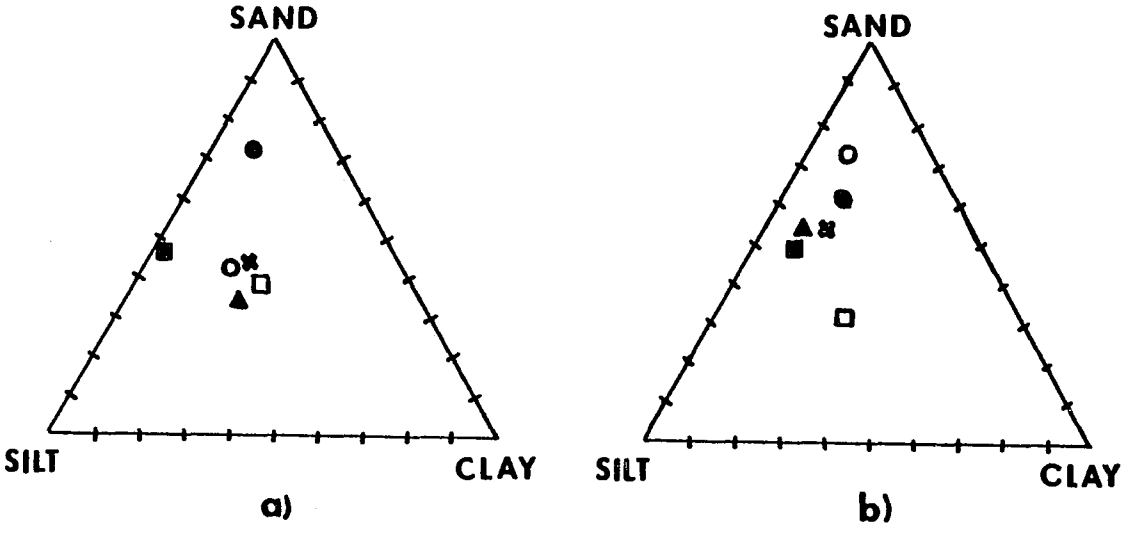

Figure 4-2. Sediment size ternary diagrams, showing relative percentages of sand, silt and clay for the five sampling sites: Site 1 (●); Site 2 (o); Site 3 (■); Site 4 (□); and Site 5 (▲). Diagram a) represents whole core average values, while diagram b) indicates values for the top 10-15 cm of sediment. Grand means for each diagram are also indicated (x).

clay), was low at this site (e.g. < 30%), and decreased with depth. Site 2 contained a high sand content in the surficial sediments (e.g. about 75%); but this fraction showed a rapid decrease with depth to values of between 20% and 40% below 30 cm. The high surface sand content at this site on the eastern side of Great Bay, may be a result of particle sorting by wind fetch across the bay from the predominantly westerly winds (see Chapter 2 for discussion). Silt and clay fractions showed parallel, increasing depth profiles at this site. At sampling location 3, depth profiles of sand, silt and clay were all nearly vertical. The only outstanding feature of the grain size analysis at this site was the very low clay content. A great deal of large pebbles in the sediments were also observed here. Site 4 was observed to contain a sand layer below 60 cm in the sediment. Above this depth, no consistent variations with depth in the percentages of sand, silt and clay were observed. At the Squamscott River location (Site 5), a sharp decrease in the percentage of sand in the sediments was observed to a depth of about 30 cm. Below this level, the sand content was relatively constant, ranging between 20 and 30%. The silt and clay fractions exhibited generally parallel depth profiles increasing with depth to about 30 cm, and relatively constant below this level.

The overall sediment type in the Great Bay Estuary has been observed to be a sandy silt (Armstrong et al., 1976; and Leavitt, 1980). This result agrees well with the sediment distribution observed at the five sites in this study (Figure 4-2). For whole core average values, Sites 2, 4 and 5 were all clustered near the mean for the five cores at about 47% sand, 35% silt and 18% clay. Site 3 had similar percentages of sand and silt; but a somewhat smaller proportion of clay (about

5%). As mentioned above, Site 1 contained a significantly higher sand content, in terms of whole core average values, than any of the other sampling areas.

A somewhat different distribution was observed in surficial sediments (Figure 4-2). The grand mean in the top 10-15 cm at these five sites was about 7% more sandy than the grand mean for the whole core average values. This reflected the higher sand content in the surface sediments at Sites 2 and 5, compared to whole core averages. In general, the areas of highest sand content, especially in the surface sediments, were those most closely associated with high flow regimes in the overlying water (e.g. Sites 1 and 2). The sampling areas with the finer sediments (e.g. Sites 3, 4 and 5), were located in the tidal flat areas of the bay.

Organic Matter and Inorganic Phosphorus. Organic carbon, nitrogen and phosphorus, and inorganic phosphorus values were determined in the sediments of all five sampling locations by methods discussed earlier (see Chapter 2). Percentages of organic carbon and nitrogen in the sediments as functions of depth are presented in Figure 4-3. Range and mean values of sedimentary organic carbon and nitrogen (SOC and SON, respectively), for each core are tabulated in Table 4-1. The range of SOC values over all of these cores was between 0.7 and 4.0%; while SON values ranged from 0.05 to 0.4%. These were within the range of values for SOC and SON in Great Bay reported by earlier workers (Armstrong et al., 1976; Lyons and Gaudette, 1979; and Leavitt, 1980). On the basis of whole core average values of SOC and SON (Table 4-1), these sites may be divided into two groups. Sites 1, 2 and 3 contained average SOC values of between 1.1 and 1.3%; and average SON values

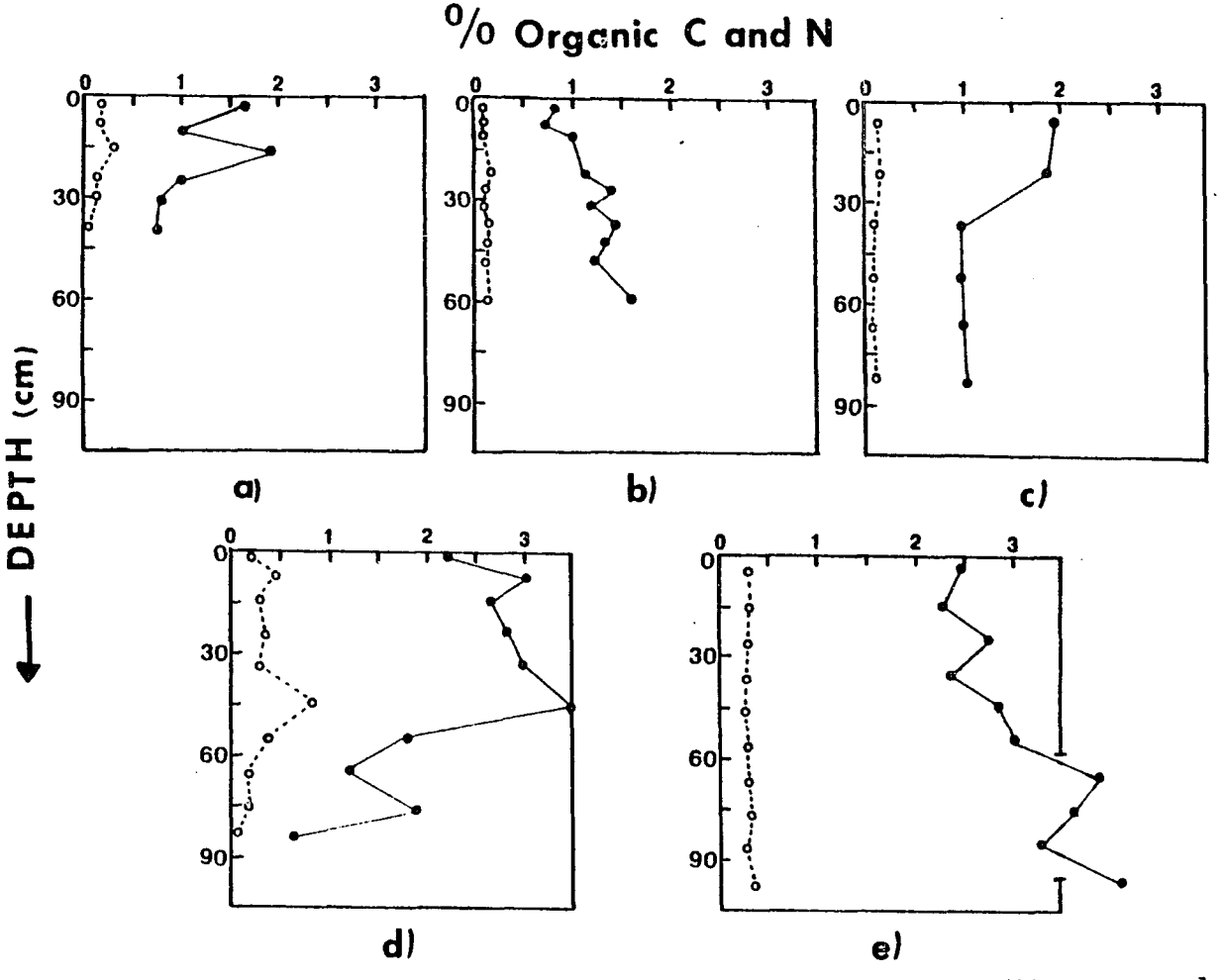

Figure 4-3. Sedimentary organic carbon and nitrogen values (%), versus depth (cm), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River).

from 0.11 to 0.14%. Significantly higher values for both SOC and SON were observed at Sites 4 and 5; with SOC between 2.2 and 3.2%, and SON from 0.29 to 0.35%. The higher organic matter content of the sediments at Sites 4 and 5 was probably due to the closer proximity of these two sites to sources of organic matter, relative to Sites 1, 2 and 3. Site 5 was located near the mouths of two major rivers emptying into Great Bay; while Site 4 was located in an eelgrass (Zostera marina), bed. Although Site 1 was also located near the mouth of a major river (e.g. the Piscataqua River), the large tidal current velocities at this sampling location would effectively preclude the deposition of light particles, which are highest in organic matter content (Sharp, 1973). Indeed, this was reflected in the high sand content at this site (see above). The location of Site 2 on the eastern side of Great Bay effectively isolated it from major sources of organic matter, since no major rivers are on the eastern shore and due to wind stress effects which sort the sediment in the overlying water such that large particles (e.g. organic poor compared to small particles), are preferentially deposited here (see Chapter 2). The low whole core average values of SOC and SON at Site 3, were primarily due to a depleted sedimentary organic matter content below 30 cm in this core (Figure 4-3). Surface values of SOC and SON at this site were similar to those at Sites 4 and 5. The depleted organic matter content of the sediments below 30 cm here may have been a result of fresh groundwater leaching of the sediments. Chloride data from this core indicated the presence of a groundwater intrusion from below (see chloride data, below). Lammela (1980), in a series of laboratory experiments has shown that distilled water may solubilize a portion of the sedimentary organic matter. In addition,

anamously high DOC values observed in the pore water from deep sections of this core support this hypothesis (see Chapter 5). However, other explanations, including a much different past depositional environment here, and bacterial degradation of SOC and SON are also possible.

Bar graph representations of sedimentary organic and inorganic phosphorus values as functions of depth for the five Great Bay sites, are illustrated in Figure 4-4. Whole core average values for these species at the various sampling locations are presented in Table 4-1. The organic phosphorus values in the sediments at Sites 1 and 4 were similar to, but somewhat lower than those obtained by Lyons and Gaudette (1979), at these same two locations. Percentages of sedimentary organic phosphorus (SOP), at the five sampling areas ranged from undetectable (e.g. < 0.0001%), to 0.02%. No significant differences among the five sampling sites in SOP content were observed. In general, SOP constituted much less than 50% of the total sedimentary phosphorus. This is in agreement with previous results from nearshore clastic sediments (Sholkovitz, 1973; Thornton et al., 1977; and Lyons et al., 1977). Ratios of inorganic/organic phosphorus (IP/OP), are listed in Appendix A. The range and mean values of IP/OP for sediments from each sampling site are summarized in Table 4-1. A grand mean of about 5 for IP/OP ratios for all sampling areas was calculated. Sedimentary inorganic phosphate (SIP), values in these cores ranged from 0.005 to nearly 0.06% (Table 4-1). Possible contributors to the SIP pool of lacustrine sediments are: phosphate sorbed to iron oxides (Harter, 1968; Williams et al., 1971a, 1971b and 1971c; and Shukla et al., 1971), phosphate sorbed to clay minerals (Gumerman, 1970; Fitzgerald, 1972; and Li et al., 1972), minerals of the apatite group (Sutherland et al., 1966; and

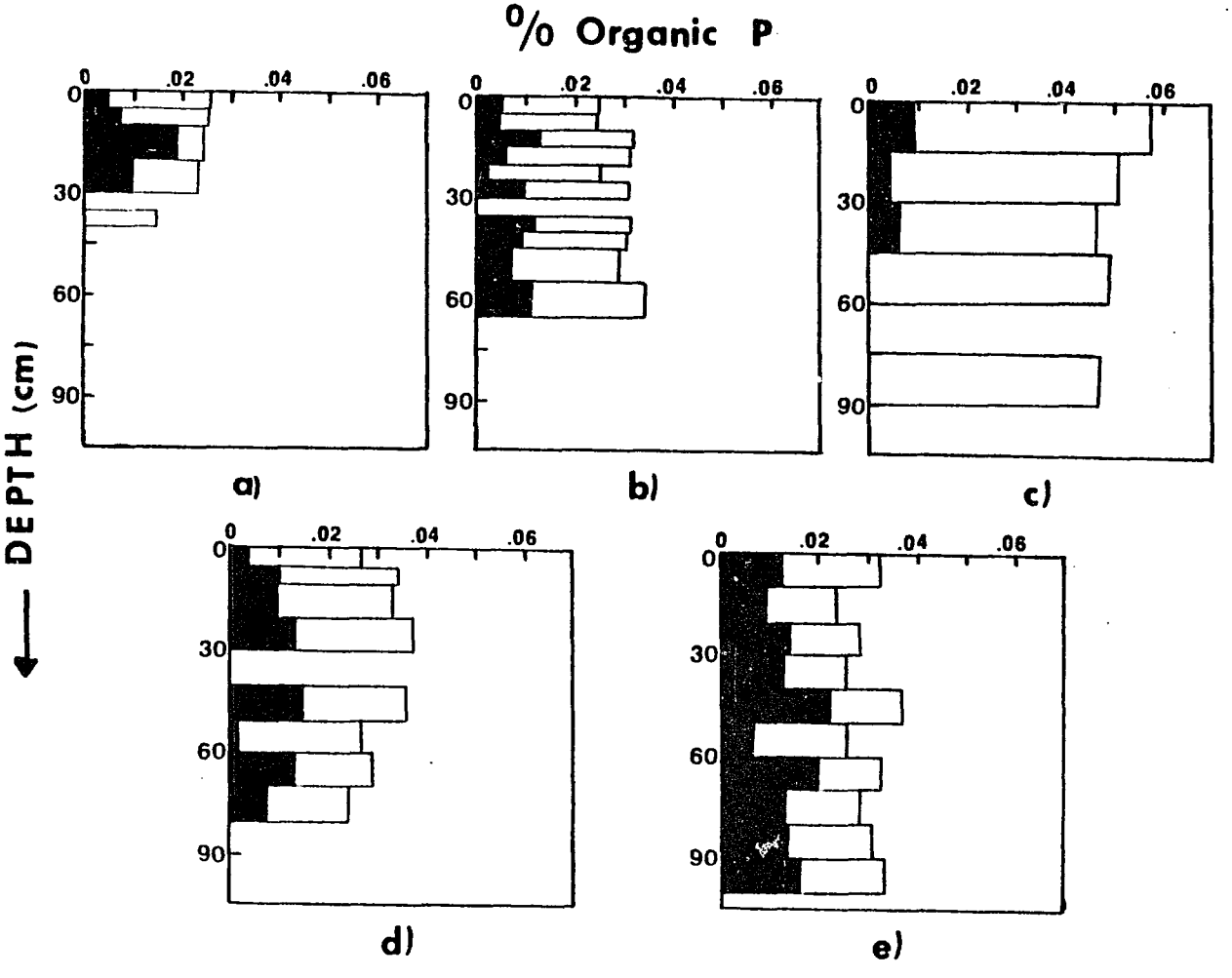

Figure 4-4. Sedimentary phosphorus values (%), versus depth (CM), at the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River). The shaded areas represent the organic phosphorus (%), and the open area the inorganic phosphorus (%).

Williams and Mayer, 1972), struvite ($Mg(NH_4)(PO_4)$), (Martens et al., 1978), and vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$) (Bray, 1973). Significantly higher values for inorganic phosphate were observed at Sites 3 and 4, based on whole core averages; however, the reasons for this lateral variability are uncertain.

Under steady state sedimentation conditions, the amounts of organic matter in the sediments would be expected to decrease with depth as a consequence of bacterial metabolic activities (Berner, 1971, and 1980). The observed depth profiles for SOC, SON and SOP showed no such systematic decrease (see Figures 4-3 and 4-4) implying that non-steady state sedimentation conditions have existed in Great Bay over the long term time scale. However, SOC and SON depth profiles in box cores from Sites 4 and 5 have shown that steady state sedimentation may occur over shorter time scales (Lyons, unpublished data). The gravity cores from Sites 2 and 5 (Figure 4-3), showed generally increasing SOC and SON percentages with depth. At Site 4, SOC and SON depth profiles increased to 45 cm; but showed a sharp decline in values below this level due to the sand layer observed here (see Figure 4-1). The increasing sand content with depth at Site 1 resulted in decreasing SOC and SON percentages. The possible influence of ground water intrusion on the SOC and SON profiles at Site 3 was discussed above. Irregular depth profiles for both SOP and SIP were observed at all of the sampling locations (Figure 4-4). Similar unsystematic depth profiles for SOP were observed by Lyons and Gaudette (1979), at Sites 1 and 4. These irregular sedimentary phosphorus depth trends were probably indicative of bacterial degradation and the myriad chemical reactions involving phosphorus in anoxic marine sediments (Bray, 1973), as well as non-

steady state sedimentation of phosphorus in Great Bay.

Correlations of % silt and clay (fines), and % organic carbon, nitrogen and phosphorus for whole core average values are presented in Figure 4-5. The inverse relationship between organic matter content and median grain size of nearshore sediments has long been known (Trask, 1939; and Revelle and Shepard, 1939). Two factors may account for this relationship: 1) organic material in seawater is light and sinks slowly, and it behaves in a manner similar to the finer mineral fractions, and 2) larger amounts of organic matter coatings are associated with finer particles (per unit weight), due to surface/volume ratio considerations (Suess, 1973). Two correlation lines are represented in plots a) and b) in Figure 4-5, and three different correlation lines in Figure 4-5c. In all of these plots, the solid lines represent correlations involving all of the points. Coefficients of correlation of 0.47 for organic carbon, 0.49 for organic nitrogen and 0.20 for organic phosphorus versus percentage fines were obtained for these plots. Elimination of the Site 1 data from the calculations, resulted in correlations indicated by the dashed lines in Figure 4-5 a), b) and c). Correlation coefficients of 0.81, 0.61 and 0.72 were obtained for plots of SOC, SON and SOP versus % fines, respectively. The better correlations observed by excluding the Site 1 data from the calculations were probably because of the much different sediment size distribution at Site 1 (see Figure 4-2a). Elimination of both the Site 1 and Site 5 data from the correlation of % SOP versus % fines resulted in the dotted line in Figure 4-5c ($r^2 = 0.97$). This may imply that Sites 2, 3 and 4 have somewhat different depositional environments for organic phosphorus than Sites 1 and 5. No correlation between whole core average values

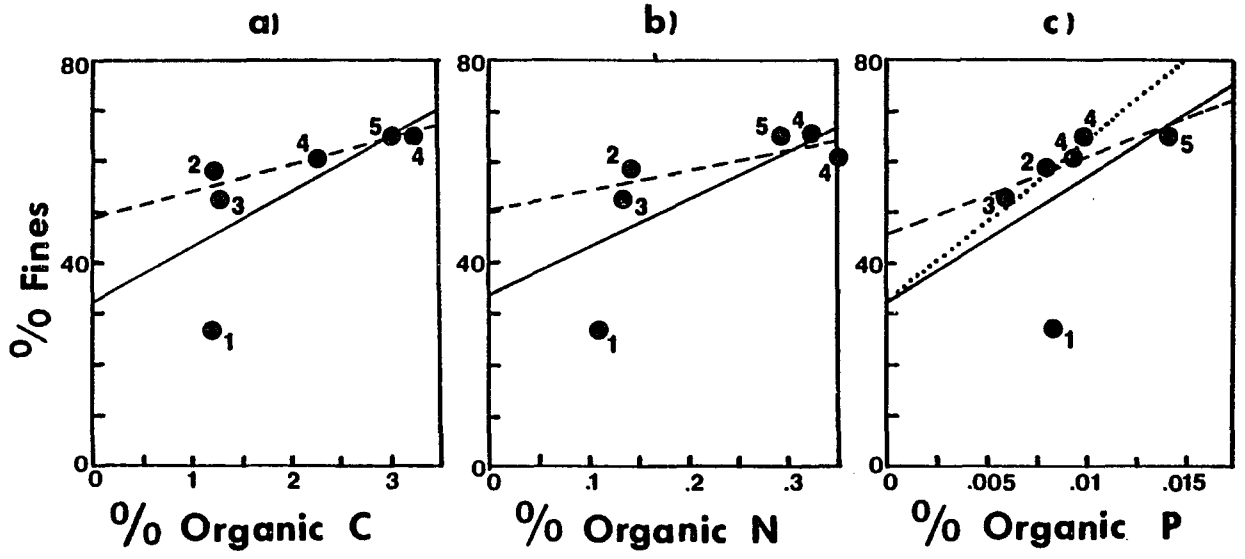

Figure 4-5. Correlations of sedimentary organic carbon (a); nitrogen (b); and phosphorus (c); versus % silt and clay (fines). The numbers next to each point indicate the sampling location, and each point represents whole core average values (see Table 4-1). The various correlation lines for each plot are discussed in the text.

of % SIP and % fines were observed.

Correlations between organic carbon, nitrogen and phosphorus and % fines in sediment sections from individual cores are presented in Figures 4-6, 4-7 and 4-8, respectively. In contrast to the relationships observed between these characteristics in whole core averages (discussed above), the correlations for sediment sections from individual cores were inconsistent. For SOC, a relationship appeared to exist with % fines at Site 2 and possibly at Sites 1 and 4 (Figure 4-6 b, a and d, respectively). These plots at Sites 3 and 5 are, essentially, scatter diagrams. Similarly for SON, relationships with % fines were observed only at Sites 1, 2 and possibly 4 (Figure 4-7 a, b and d, respectively). No correlation between SOP and % fines was observed in any core (Figure 4-8). This general lack of correlation between organic matter content and sediment size in individual cores over time (represented by depth), suggests that factors other than those controlling sediment size are affecting the organic matter content of Great Bay sediments. These factors may include estuarine productivity and the types and rates of diagenetic remineralization of sedimentary organic matter. These factors are apparently averaged when whole core average correlations of % SOC, SON and SOP versus % fines are considered. No correlation between % SIP and % fines was observed in any individual core.

The molar ratios of C, N and P in sedimentary organic matter from the five Great Bay sampling locations are tabulated (with depth), in Appendix A. Whole core average values and ranges of these ratios are presented in Table 4-1. Organic carbon/organic nitrogen ratios (OC/ON), in these sediments ranged from 4.75 to 16.9, and had an overall

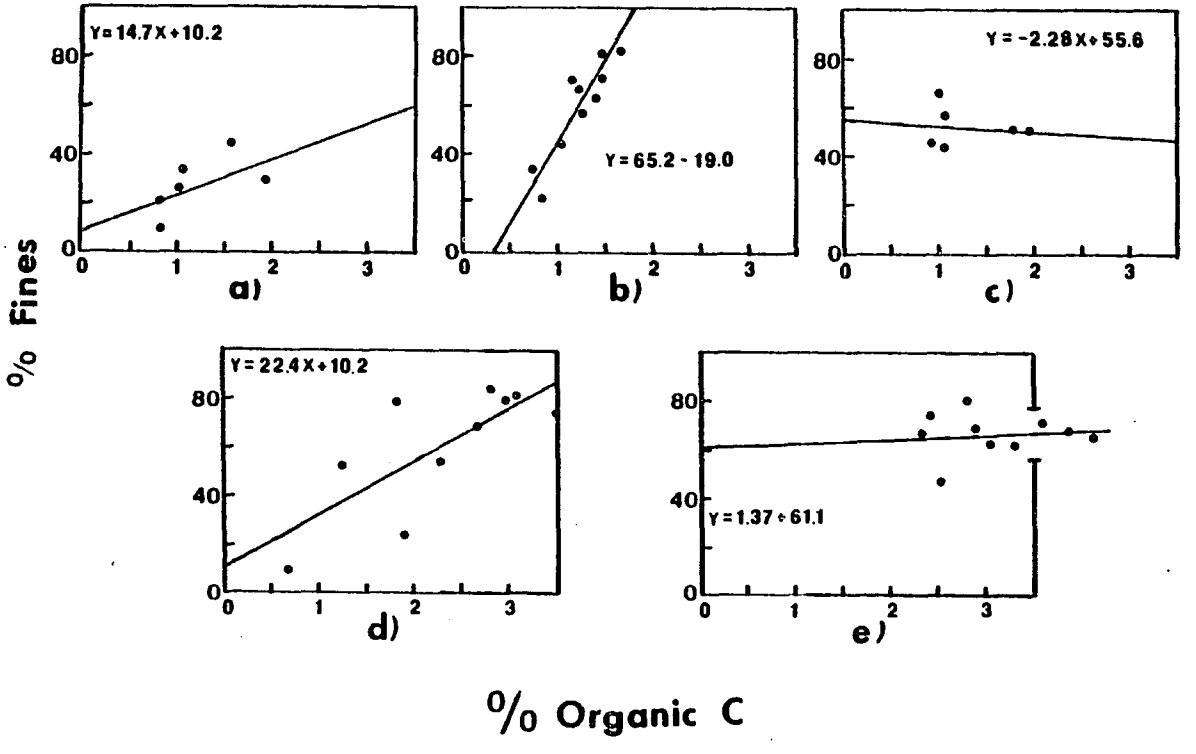

Figure 4-6. Correlation of sedimentary organic carbon (%), versus % silt and clay (fines), for the five Great Bay sites: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River). Theoretical lines are presented in each plot. Calculated correlation coefficients for each plot were: a) 0.368; b) 0.846; c) 0.0189; d) 0.590; and e) 0.00909.

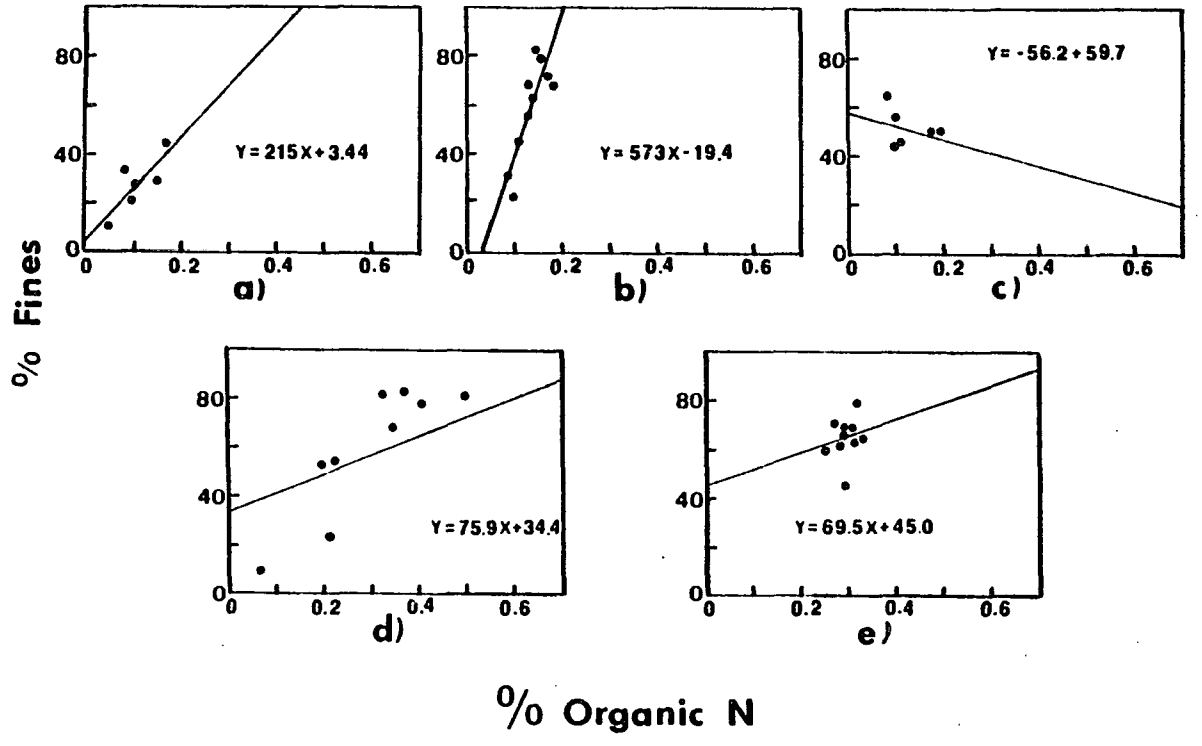

Figure 4-7. Correlation of sedimentary organic nitrogen (%), versus % silt and clay (fines), for the five Great Bay sites: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River). Theoretical lines are presented in each plot. Calculated correlation coefficients for each plot were: a) 0.707; b) 0.729; c) 0.0889; d) 0.407; and e) 0.0375.

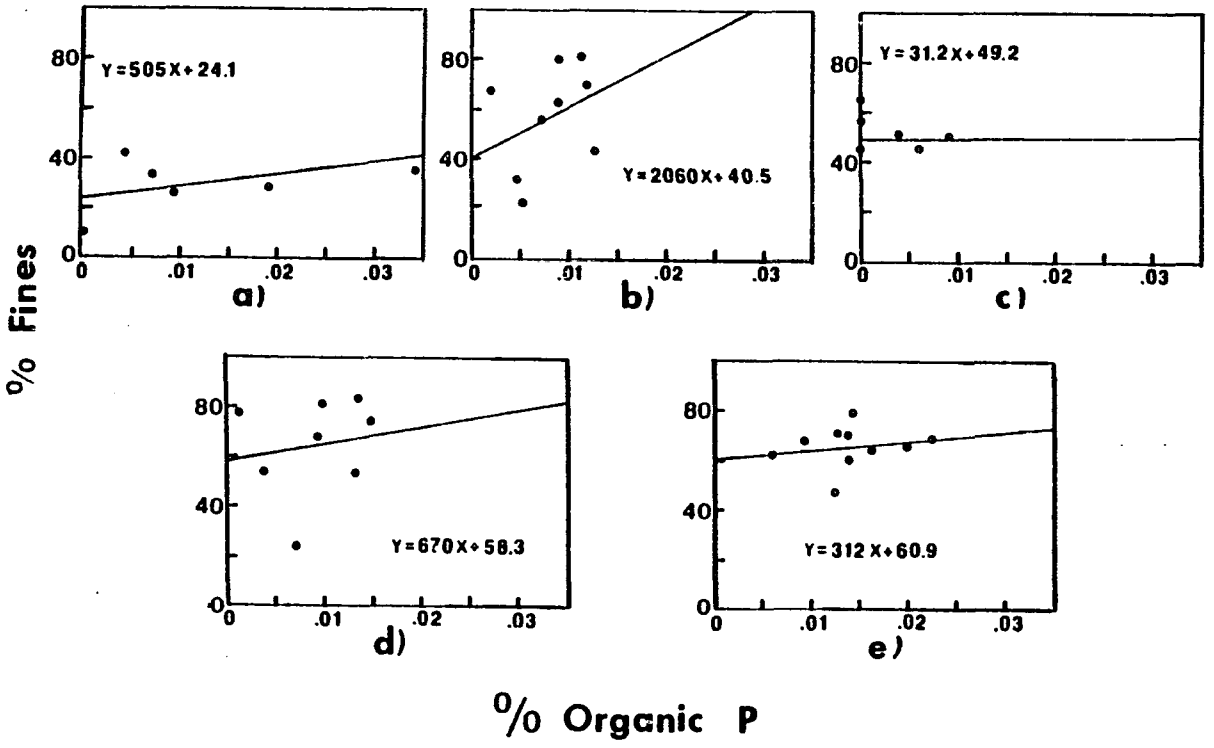

Figure 4-8. Correlation of sedimentary organic phosphorus (%), versus % silt and clay (fines), for the five Great Bay sites: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River). Theoretical lines are presented in each plot. Calculated correlation coefficients for each plot were: a) 0.0882; b) 0.131; c) 0.000726; d) 0.0269; and e) 0.0303.

average value of 10.9. Only two sediment sections (both from Site 4, in an eelgrass bed), had OC/ON values less than the Redfield ratio of 6.6 (Redfield, 1958).

Two factors may account for OC/ON ratios in estuarine sediments greater than the Redfield value: 1) inputs of terrestrial organic matter (with its lower N content), to estuarine sediments and 2) preferential utilization of N containing compounds by bacteria during early diagenesis in the sediments. Organic carbon/organic phosphorus (OC/OP), and organic nitrogen to organic phosphorus (ON/OP), ratios were also observed to be generally greater than the corresponding Redfield values of 106 and 16. Indeed, the OC/OP and ON/OP ratios imply that these sediments are considerably more depleted in organic phosphorus than in organic nitrogen. Organic carbon/organic phosphorus ratios ranged from 200 to 4,000, with an overall mean value of 780. Organic nitrogen/organic phosphorus ratios in these cores varied from 17 to 770, and had an overall mean of 81. The OC/ON, OC/OP and ON/OP ratios observed in Great Bay sediments during this study are similar to values published for other estuarine sediments (Rittenberg et al., 1955; Nissenbaum and Kaplan, 1972, Carter and Mitterer, 1978; Lyons and Gaudette, 1979; and Rosenfeld, 1981).

Considerable variability in all of the organic matter molar ratios was observed in each core. As a result of this, although whole core average OC/ON, OC/OP and ON/OP ratios varied considerably from site to site, these differences were not significant (see Table 4-1). Organic carbon/organic nitrogen ratios were observed to increase irregularly with depth at Sites 1, 2 and 5. This has been interpreted as resulting from preferential decomposition of organic nitrogen compounds

(Rosenfeld, 1981), although the existence of a different depositional environment in the past cannot be ruled out. No changes with depth in the OC/ON ratio were observed at Sites 3 and 4. In addition, OC/OP and ON/OP values showed no depth variation at any site. The lack of any vertical change in the OC/OP and ON/OP ratios of these sediments probably resulted from the complex chemistry of phosphorus in anoxic marine sediments (Bray, 1973), and the apparent non-steady state accumulation of Great Bay sediments and organic matter.

B. Inorganic Species in Pore Water

Titration Alkalinity and pH. Values of titration alkalinity versus depth for deep cores from Sites 1, 3, 4 and 5 in Great Bay are presented in Figure 4-9. No data were available for Site 2. All of these cores were collected during the summer months. Increasing alkalinities with depth were observed at all the sampling locations, except Site 3 (Adams Cove). These results agree with previous measurements of alkalinity in anoxic marine pore water by other workers (Sayles et al., 1970; Manheim et al., 1970; Berner et al., 1970; Gieskes, 1972; Troup, 1974; Martens and Goldhaber, 1978; and Lyons, 1979). Titration alkalinities in the pore water of Great Bay were considerably higher than overlying seawater values (1-3 meq/l). Concentrations up to 70 meq/l were observed at Site 4. This represents one of the highest titration alkalinities ever reported for anoxic marine pore water. The high titration alkalinity of pore water (relative to overlying seawater values), has been attributed to buildup of the byproducts of bacterial decomposition of organic matter (Berner et al., 1970; Gieskes, 1972; and Hines, 1981). However, inorganic reactions such as the precipitation or dissolution of $CaCO_3$, and reverse weathering of silicate min-

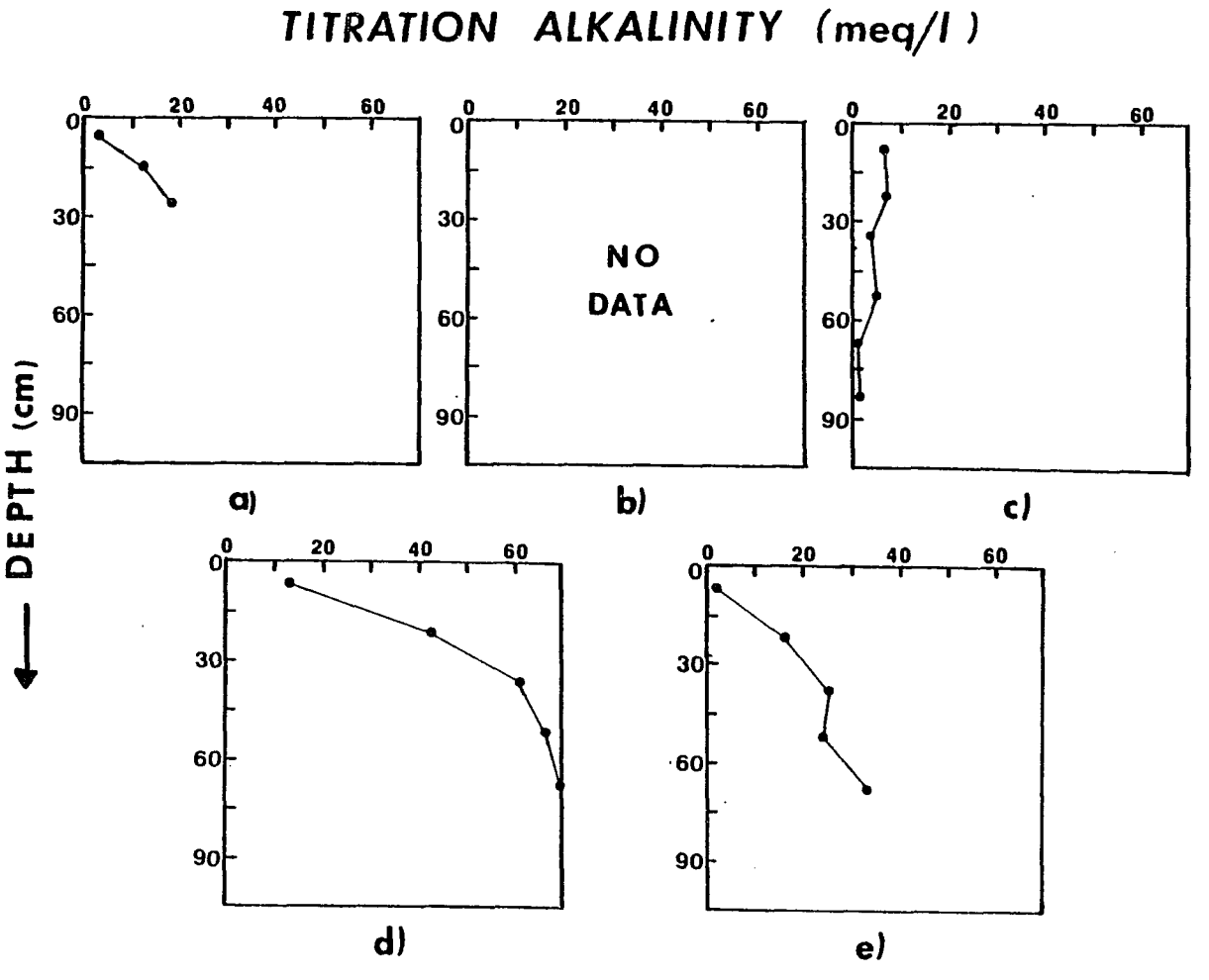

Figure 4-9. Titration alkalinity (meq/l), versus depth (cm), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and Site 5 (Squamscott River).

erals may also contribute to pore water alkalinities in certain sedimentary environments (Berner et al., 1970). In Great Bay, increases in the pore water alkalinities are correlated with concomitant increases in ammonia and phosphate (see results below), implying bacterial production for the observed trends. Differences in the titration alkalinity values at the four sampling sites (Figure 4-9), probably reflect differences in bacterial activities at these locations. Bacterial activities, in turn, are likely linked to differences in the amounts and nature of the organic matter at the various sampling sites (Hines, 1981).

As discussed earlier (Chapter 3), a number of chemical species may contribute to the titration alkalinity of anoxic pore water. However, in most sedimentary environments HCO_3^- predominates (Gieskes, 1972). The series of alkalinity titration curves of pore water from Site 5 (Figure 4-10), substantiate this view. In these plots, the dominance of a single inflection point is evident. However, pKa values calculated from these plots (ranging from 6.47 in the 0-15 cm section, to 7.03 at 75-90 cm), were somewhat higher than the theoretical pKa for the reaction:

$$H_2CO_3^* + H_2O = H_3O^+ + HCO_3^-$$

which is in the range of 6.20 to 6.35 for the temperature and salinity conditions of these pore water samples (Stumm and Morgan, 1970). The difference between the theoretical and observed pKa values may reflect the influence of other conjugate bases in the pore water (e.g. NH_3, $H_2PO_4^-$, HPO_4^{2-} and HS^-). Indeed, there are indications of secondary inflection points in many of the titration curves in Figure 4-10.

In addition to vertical and lateral variability, titration alkalinity values in Great Bay anoxic pore water also exhibited a dis-

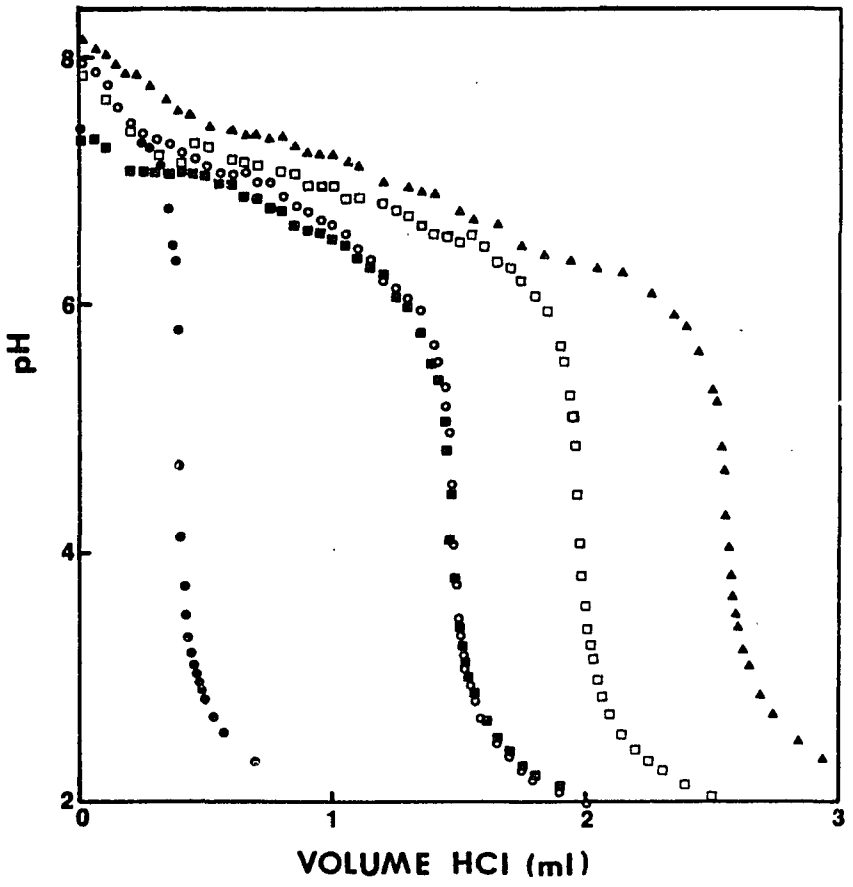

Figure 4-10. Pore water alkalinity titration curves for a gravity core from Site 5 (5-15-81). Each curve is for pore water from a different sediment section: 0-15 cm (●); 15-30 cm (o); 30-45 cm (■); 45-60 cm (□); and 75-90 cm (▲). The titrant was 0.01 M HCl.

tinct seasonal trend. These data are illustrated for gravity cores and box cores in Figures 4-11 and 4-12, respectively. In the gravity cores, a dramatic increase in values of titration alkalinity at all depths was observed between June and August. For example, at 60-75 cm a more than 2.5 fold increase in titration alkalinity was observed. Such a large increase is not attributable to sampling variability (see Chapter 2). This increase in pore water titration alkalinity values during the summer months correlates with observed increases in bacterial activities over this period (Hines, 1981; and Westrich and Berner, 1981). Between August and October, a decrease in titration alkalinities at all depths was observed at this site (Figure 4-11). Interestingly, the June and October cores exhibited nearly identical depth profiles. The observed decrease in alkalinities was probably a result of lower bacterial activities in the fall. This reduction in microbial metabolism probably resulted from two environmental effects: 1) reduced temperatures in the autumn, and 2) the buildup of toxic substances (e.g. H_2S), in the pore water (Hines, personal communication). Observed alkalinity values represent 'snapshots' at points in time of the production/removal steady-state for this chemical species. Lower rates of bacterial activity in the fall (e.g. decreased production), result in the establishment of new steady-state conditions by removal processes (e.g. lower titration alkalinity values). Removal processes for alkalinity in pore water include molecular diffusion, precipitation from solution, adsorption on sediments and others (Berner, 1980). Temperature may also have an influence on these removal processes (e.g. by affecting diffusion and the solubility of various carbonate mineral species), in addition to its effect on bacterial activity. The details of these processes and

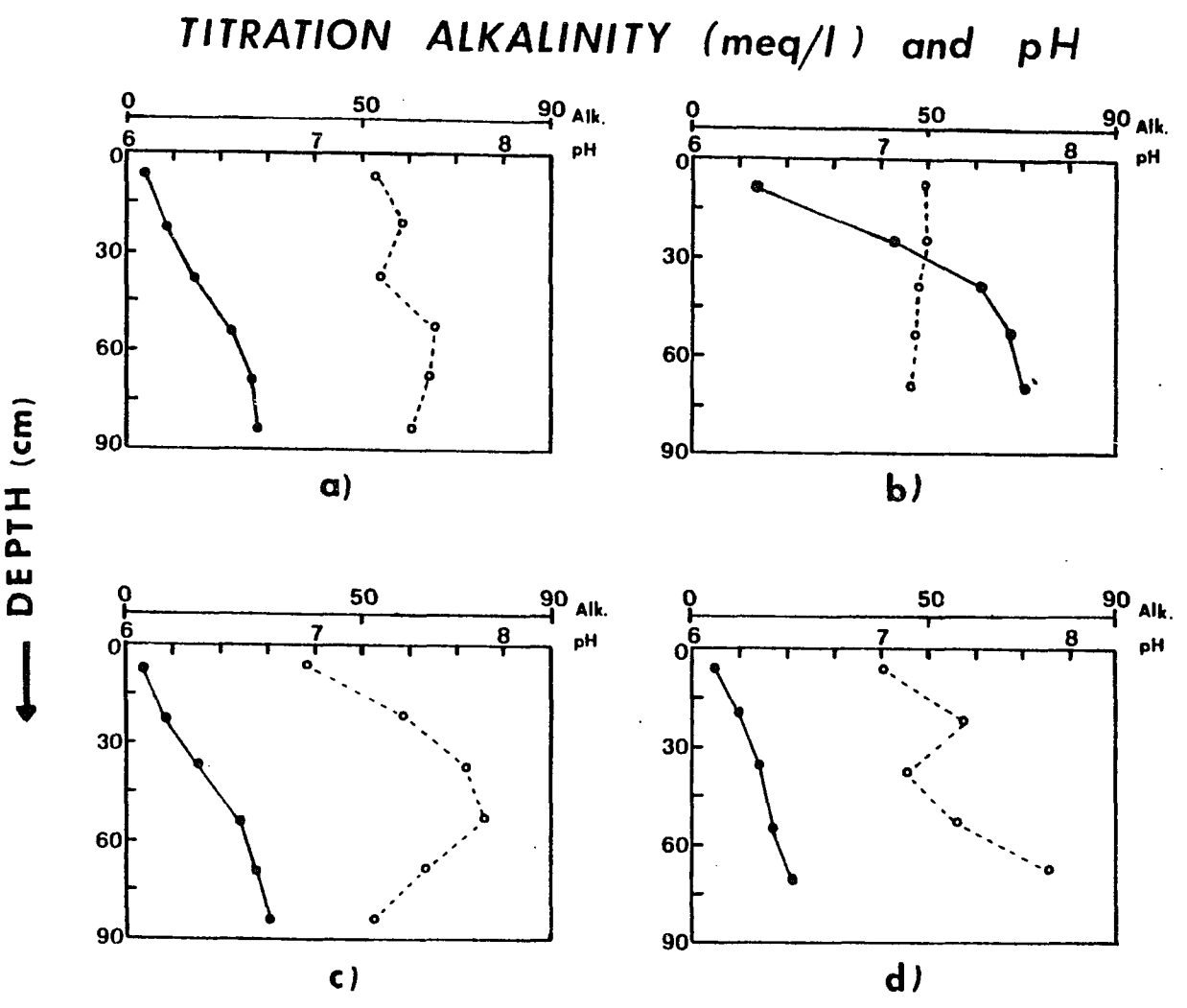

Figure 4-11. The seasonal variation of titration alkalinity (meq/l), (●—●), and pH (o---o), in gravity cores from Site 4 (Footman Islands): a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); c) Core OAX-II (10-21-80); and d) Core UF-IX (4-15-81).

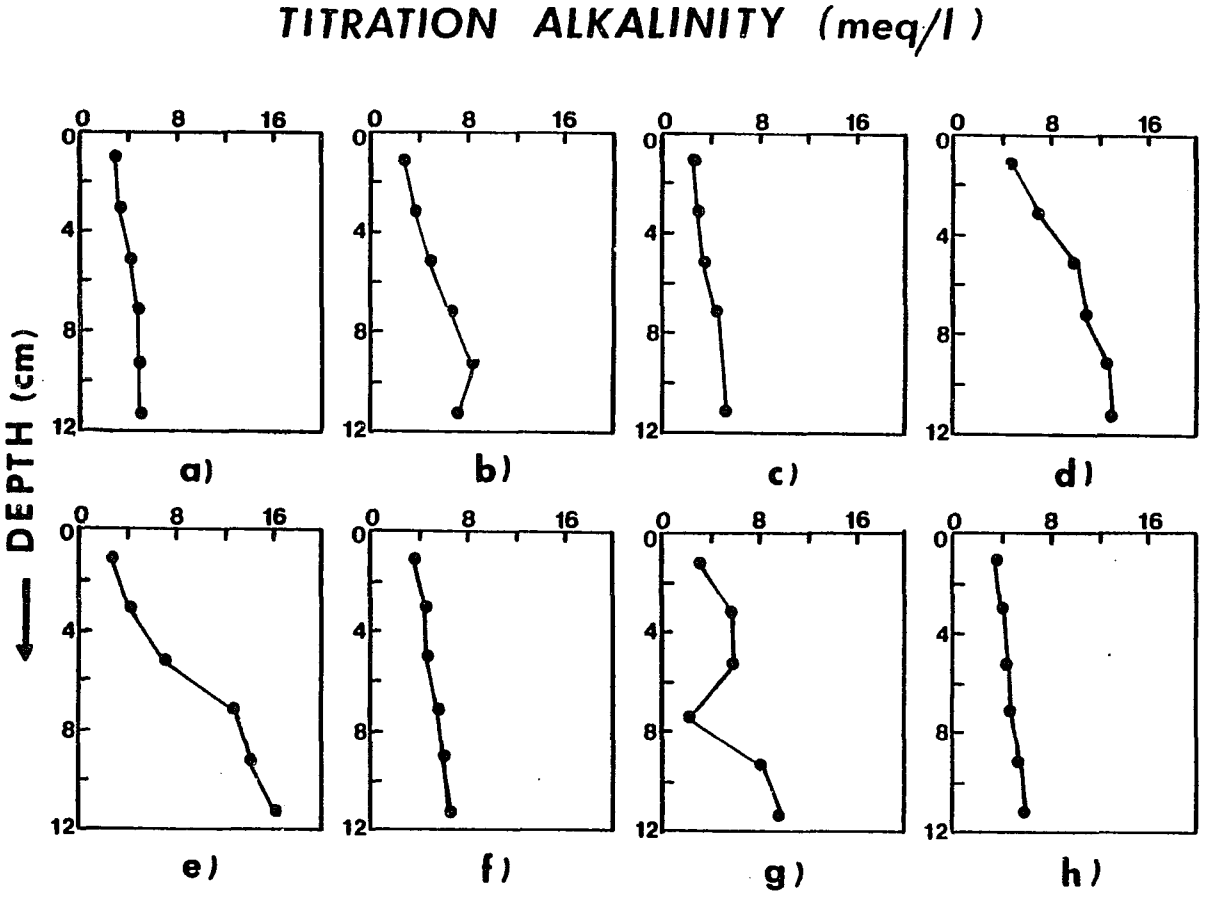

Figure 4-12. The seasonal variation of titration alkalinity (meq/l), in box cores from Site 3 (Adams Cove): a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

their effects on the seasonal variability of titration alkalinity in estuarine pore water must await further work.

Titration alkalinity values in box cores from Site 3 (Adams Cove), showed a qualitiatively different seasonal trend than gravity cores (Figure 4-12). Alkalinities were observed to increase in the pore waters of these box cores through the spring. June values of titration alkalinity in the bottom two sections of the box core were up to three times the corresponding March values. Hines (1981), has observed an increase in both sulphate reducing and total heterotrophic bacterial activities over this same period in these cores. This implies a bacterial source for the increasing alkalinity values observed. The activities of sulphate reducing and total heterotrophic bacteria were observed to continue to increase through the summer months in these cores (Hines, 1981). However, titration alkalinity values showed a dramatic decline over this period from the high early June levels. This is in contrast to what was observed in gravity cores, where maximum titration alkalinities were observed in August, as discussed above. Similar seasonal trends in shallow box cores from nearshore sedimentary environments have been previously observed (Aller, 1977; Goldhaber et al., 1977 and Aller, 1980). The dramatic decline in pore water species from these nearshore sediments during the summer months, despite continued high bacterial activities, has been attributed to intensive reworking of surficial sediments by macrobenthic organisms (e.g. bioturbation), (Aller, 1977; Aller, 1978; Aller and Yingst, 1978; and Hines, 1981).

Bioturbation may occur in two basic modes (Aller, 1977; and Berner, 1980). Some benthic organisms (e.g. snails and mud crabs), mix surficial sediments by simply moving through them. This process may

reach to tens of centimeters in the sediments, and result in the mixing of pore water and overlying seawater. A second type of bioturbation routinely encountered in nearshore marine sediments involves tube dwelling organisms (e.g. polychaete worms and bivalves), and is most easily described as resulting from changes in the geometry of molecular diffusion in the sediments (Aller, 1978). This form of bioturbation, usually called irrigation, may also reach to tens of centimeters in the sediments, and results in increased diffusion of dissolved species from the pore water to the overlying seawater. More detailed discussions of bioturbation have been presented elsewhere (Rhoads, 1962, 1973, 1974 and 1976; Cullen, 1973; Johnson, 1974 and 1977; Rhoads et al., 1977; Aller, 1977; Aller, 1978; and Aller and Yingst, 1978). Previous studies of bioturbation in Great Bay have indicated that this process normally extends from June to December, and may reach a depth of 15 cm (Armstrong et al., 1979; Hines, 1981; Lyons, personal communication). Moreover, a study in Great Bay has shown that the degree of bioturbation is directly correlated with salinity (Winston and Anderson, 1971). Thus, the effects of bioturbation on the pore water chemistry should be more pronounced at Site 3 than at Site 5; and this has been observed (Lyons et al., 1979b; and Hines, 1981). Winston and Anderson (1971), have determined the molluscs Gemma gemma and Macoma balthica to be primarily responsible for bioturbation near Site 3 in the summer, and the polychaete Nereis sp. to be the dominant bioturbator farther down bay (e.g. near Site 1). The process of bioturbation may be an important factor in the cycling of a number of elements for three reasons: 1) it increases the flux of chemical species across the sediment water interface (Aller, 1977), 2) enhances the bacterial degradation of organic matter

Goldhaber et al., 1977; and Hines, 1981), and 3) may result in oxidation effects (e.g. removal of iron from the pore water), (Hines, 1981).

The titration alkalinity depth profile in the November box core (Figure 4-12), was similar to that observed during the preceeding March. These alkalinity values were considerably lower than those observed in the August box core. These lower alkalinities in the fall and early spring, relative to summer values, were likely the result of decreased bacterial activities caused by the lower water temperatures during the cooler months of the year. A similar effect was observed in the gravity core samples discussed earlier. The similarity of the March and November alkalinity profiles suggests that these limiting values and an almost vertical profile are maintained throughout the winter months.

A somewhat different seasonal trend for titration alkalinity was observed in box cores from Site 4 (Footman Islands). These data are tabulated in Appendix B. At this sampling location, alkalinities were observed to gradually increase from April to September; with no pronounced summer decrease due to bioturbation, as observed at Site 3 (Adams Cove). Alkalinity values, particularly in the deeper sections of the box cores from Site 4, were considerably lower than those observed at Site 3. This is a puzzling result, since the gravity core data discussed earlier showed much higher alkalinity concentrations at Site 4. In addition, other comparative data (e.g. pore water concentrations of ammonia, phosphate and dissolved organic carbon, and sedimentary C, N and P contents), from gravity cores indicate generally higher heterotrophic bacterial activities at Site 4, relative to Site 3. The anamolously low alkalinities observed in the upper 12 cm of sediment from Site 4 may result from enhanced removal of HCO_3^- from the

pore water by eelgrass (Zostera marina), roots. Thus, despite higher bacterial activities and production of titration alkalinity in the sediments of Site 4, lower alkalinities would be observed in the pore water as a result of assimilation by the eelgrass if this hypothesis is correct. Eelgrass has previously been shown to effect the concentration of inorganic nitrogen species in pore water (Short, 1981).

The pH values of wet sediments from four Great Bay sites as functions of depth are illustrated in Figure 4-13. These profiles are from the same gravity cores as those discussed earlier (Figure 4-9), for titration alkalinity. In all of these cores pH values ranged between 7 and 8. Earlier workers have predicted that the lower limit of pH in anoxic marine sediments should range between 6.6 and 6.9 controlled by iron sulphide precipitation (Gardner, 1973; and Ben Yaakov, 1973). Ben Yaakov (1973), has also suggested that the upper limit of pH in this environment is controlled by the precipitation of $CaCO_3$, and should not exceed 8.3. However, these predictions may be an oversimplification of the situation, since they fail to take into account the net consumption of CO_2 that takes place during methanogenesis (Claypool and Kaplan, 1974), and the effect the high concentrations of organic acids in the pore water may have on the pH (Willey et al., 1975). In addition, the potential buffering effects of silicate minerals has not been addressed (Sillen, 1961; Holland, 1965; Garrels, 1965; and Pytkowicz, 1967). Whatever the ultimate controlling factors, the pH values of Great Bay anoxic sediments are consistent with the range of pH obtained by other workers in similar sedimentary environments (Rittenberg et al., 1955; Ruburgh, 1969; Nissenbaum et al., 1972; Troup, 1973; Martens and Goldhaber, 1978; Martens et al., 1978; and

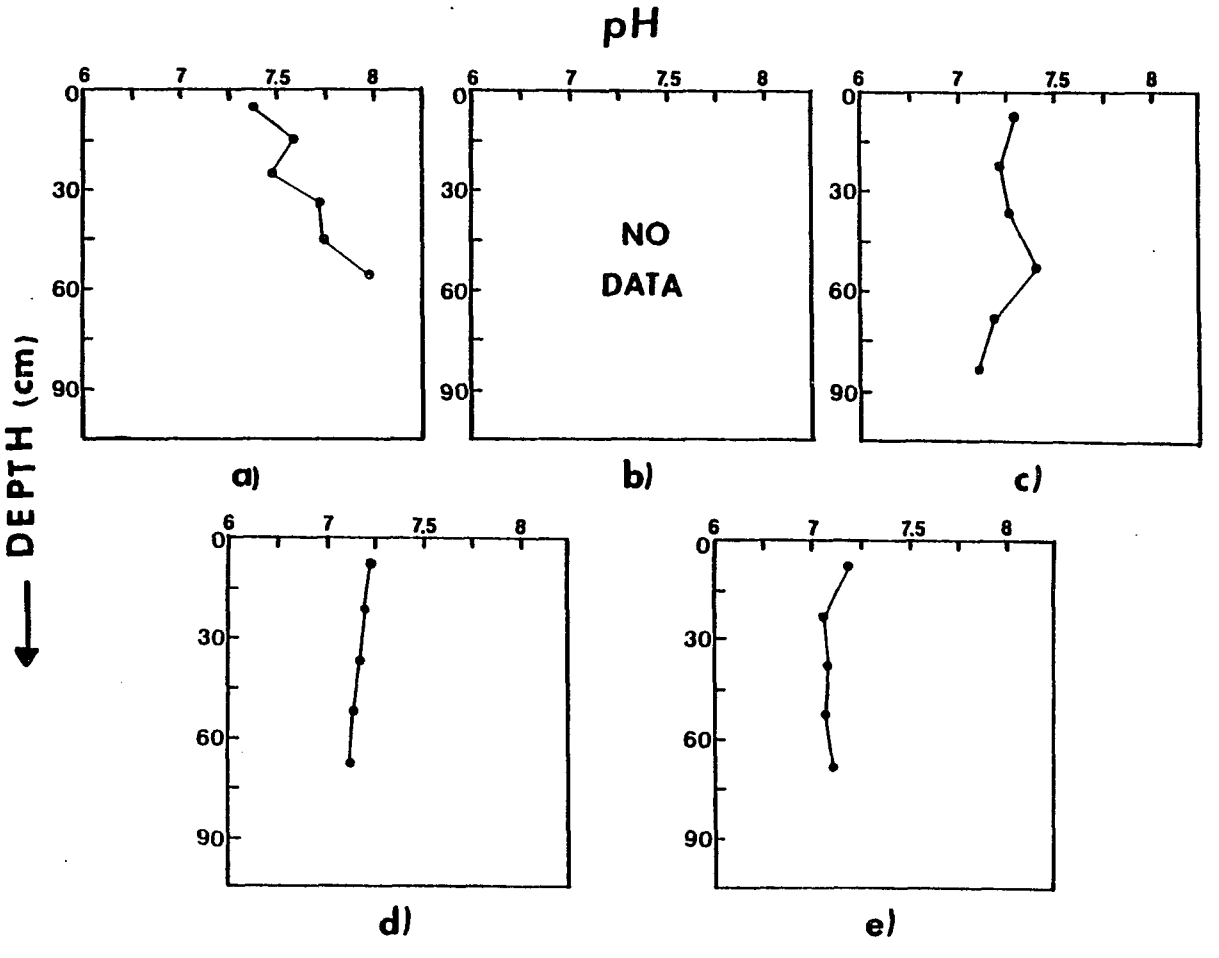

Figure 4-13. Values of pH versus depth (cm), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River).

Lyons, 1979).

The pH depth profiles in these cores showed no general systematic trend. At Site 1, pH's were observed to increase with depth; while at the other three sampling locations in Figure 4-13, little vertical pH variation was seen. Other workers have also observed little change in the pH of anoxic marine sediments with depth (Reeburgh, 1969; Troup, 1973; Martens et al., 1978; and Lyons, 1979). However, Martens and Goldhaber (1978), observed decreasing pH with depth in the sediments of the White Oak River Estuary, North Carolina. This type of profile may have resulted from the net acid production of heterotrophic bacterial activities in anoxic marine sediments, such as in the following reaction:

$$(CH_2O)_{106}\ (NH_3)_{16}\ H_3PO_4 + 53\ SO_4^{2-} =$$

$$106\ HCO_3^- + 53\ HS^- + 16\ NH_4^+ + HPO_4^{2-} + 39\ H^+$$

However, the pH of a particular sediment and the observed depth profile seem to result from a number of interacting factors, whose relative importance is difficult to assess.

Whole core average pH values were observed to decrease steadily in an up bay direction, ranging from 7.65 at Site 1 to 7.11 at Site 5. This trend is probably a consequence of the higher production of protolytic species from bacterial diagenetic processes at the up bay locations. The higher concentrations of ammonia, phosphate, titration alkalinity and dissolved organic carbon in the pore water at Sites 4 and 5, relative to the farther down bay sampling sites, supports this idea. Martens and Goldhaber (1978), observed a similar trend of decreasing pH in an up bay direction in the White Oak River Estuary, North Carolina.

The seasonal variation of pH in four gravity cores from Site 4 (Footman Islands), is illustrated in Figure 4-11. Values of pH in the August core were, on average, less than those for June, October and April. This was not a surprising result, since the activities of heterotrophic bacteria in the sediments (and, consequently, the production of protolytic chemical species), are highest in the summer months (Hines, 1981; and Westrich and Berner, 1981). Seasonal changes in the shape of the pH depth profile were also observed in these cores. In the August core, this profile was virtually straight up and down, while during other times of the year a general increase in pH with depth was observed. The nearly vertical profile for pH versus depth in the August core may indicate the influence of a mechanism for the regulation of the lower limit of pH, as discussed earlier. Alternatively, this trend may reflect the establishment of steady-state conditions at various depths between the production of protolytic chemical species by bacteria, and removal processes (e.g. diffusion, precipitation and adsorption). The explanation for the pH increases with depth in the April, June and October cores is uncertain, but this again may reflect the establishment of steady-state conditions at various depths between production and removal processes.

The seasonal changes of pH in box cores from Site 3 (Figure 4-14), closely paralleled those observed in gravity cores. Whole core average pH's were observed to decrease from March through June as a result of increasing bacterial activities over this period. The lowest pH's were observed in June, with slight increases in pH observed in the July and August cores. These somewhat higher summer pH values were probably a consequence of the transport of overlying seawater into the

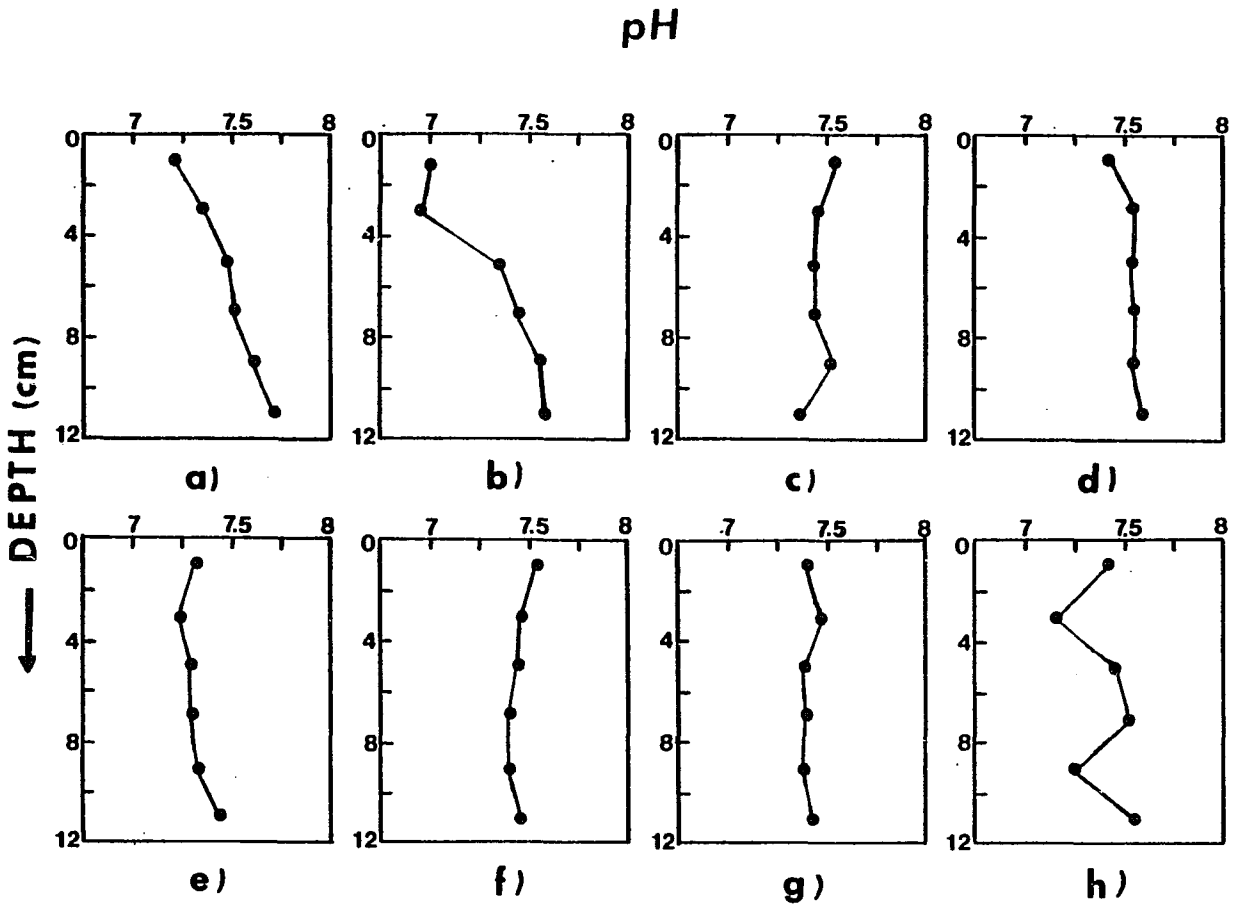

Figure 4-14. The seasonal variation of pH in box cores from Site 3 (Adams Cove): a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

sediment by bioturbation. Seasonal changes in the shape of the pH versus depth profiles in these box cores were also similar to those observed in the gravity cores. Over the period March through May, the pH versus depth profile was observed to change from a convex shape (i.e. increasing pH with depth), to a nearly vertical profile. This vertical line profile of pH versus depth was maintained through the summer months. Possible explanations for these observed seasonal trends were discussed above.

Values of pH in a series of box cores from Site 4 (Footman Islands), are tabulated in Appendix B. These pH's were within the range of values observed in other cores from Great Bay. However, pH values in the box cores from Site 4 were on average, lower than those observed in box cores from Site 3. This is similar to the lateral variability observed in gravity cores from Sites 3 and 4 discussed above, and may be indicative of higher bacterial activities and concomitant greater acid production at Site 4. In contrast to what was observed in box cores from Site 3, no systematic depth or seasonal trends were observed in the box cores from Site 4. This may reflect the influence of eelgrass on protolytic chemical species in the pore water.

Chloride and Sulphate. Concentration versus depth profiles for chloride and sulphate from the same gravity cores presented earlier for pH and alkalinity at four Great Bay sites, are illustrated in Figure 4-15. The chloride profiles at Sites 1, 4 and 5 were nearly vertical, with chlorinities ranging between 15 and 16 $^{o}/_{oo}$ at Site 1, 13 and 14 $^{o}/_{oo}$ at Site 4, and 12 and 14 $^{o}/_{oo}$ at Site 5. These pore water chlorinities were somewhat lower than those observed in the overlying seawater during this time of year (15-16 $^{o}/_{oo}$). However, these lower

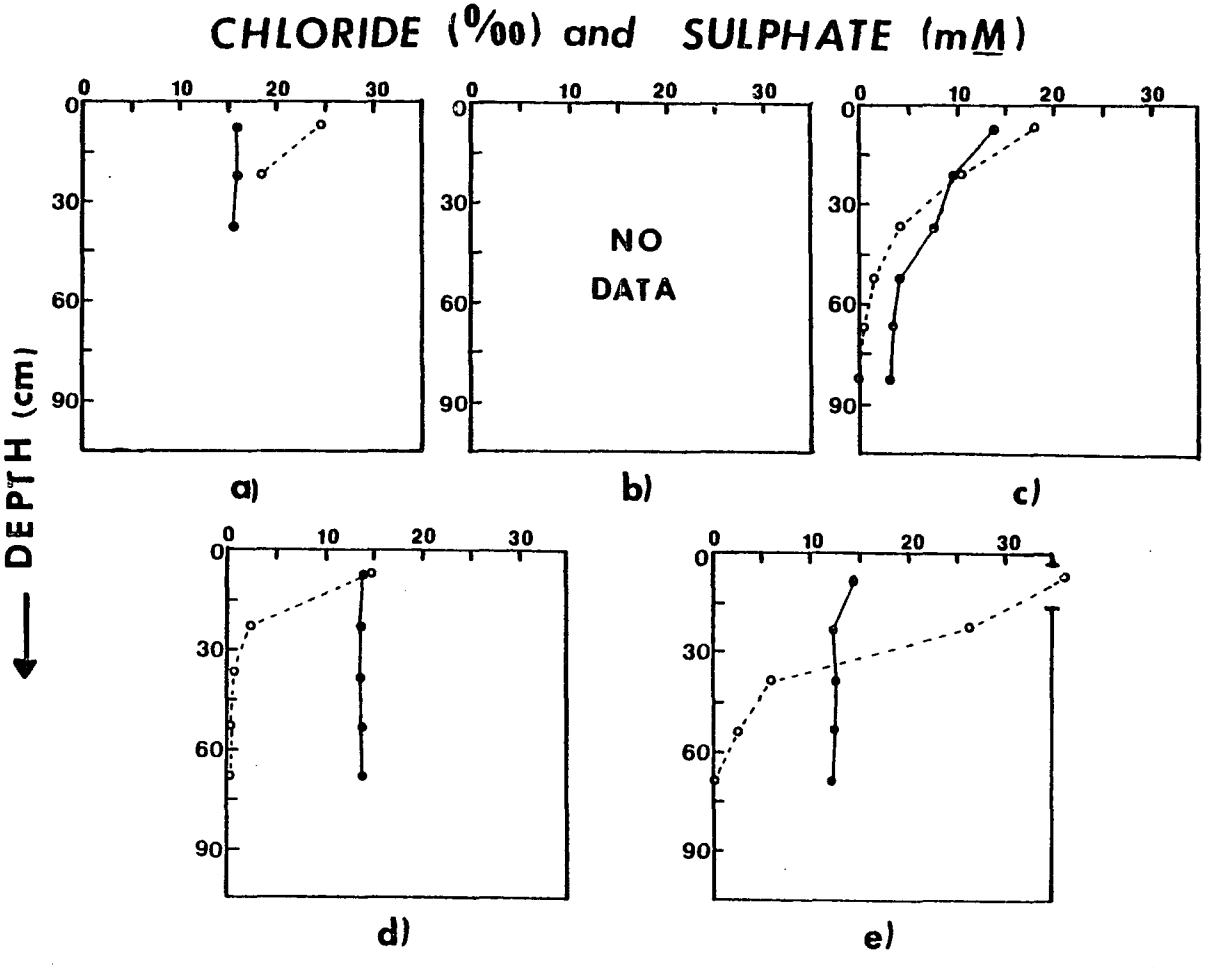

Figure 4-15. Chloride (°/oo), (•—•), and sulphate (mM), (o---o), versus depth (cm), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River).

pore water values were probably not a result of any diagenetic reactions involving chloride, but rather point to the slow rates of overlying water penetration via diffusion into the sediments. Similar vertical depth profiles for chloride have been observed by other workers (Siever et al., 1963; Sanders et al., 1965; Troup, 1974; Manheim, 1976, and Gaudette and Lyons, 1980), indicating the general nonreactivity of chloride in anoxic marine sediments. The depth profile for chloride at Site 3 (Figure 4-15c), showed a decrease in chlorinity from about 14 °/oo in the top 15 cm of sediment to 3 °/oo in the 75 to 90 cm sediment section. This is suggestive of fresh groundwater intrusion at this site. The diluting effect of the groundwater was also evident in the titration alkalinity results from this core discussed earlier.

The sulphate concentrations of these cores were observed to decrease with depth at all sites (Figure 4-15). The depletion of sulphate in the pore water of anoxic marine sediments is primarily a result of bacterial sulphate reduction, (see Chapter 1). At Sites 3, 4 and 5 sulphate concentrations were observed to reach zero at depths of 80 cm, 35 cm and 70 cm, respectively. This may indicate that higher rates of sulphate reduction exist at Site 4. Sulphate was also observed to decrease with depth at Site 1, however, due to the existence of a sand layer below 45 cm at this location, the concentration never reached zero. Similar sulphate versus depth profiles at Sites 1 and 4 in Great Bay were observed by Lyons and Gaudette (1979). The observed sulphate profile at Site 3 is complicated by the intrusion of fresh groundwater, as indicated by the chloride depth profile discussed above. This fresh water intrusion resulted in dilution of the pore water, and the decreasing chloride and sulphate concentrations with depth that were

observed. However, sulphate/chloride ratios for this core decreased with depth, indicating that the observed depth profile for sulphate was not a result of dilution alone (i.e. sulphate reduction is occurring).

Sulphate/chloride ratios for the cores in Figure 4-15 ranged from 0 to 0.243, compared to a ratio of 0.140 for standard ocean water (Riley and Chester, 1971). In all of these cores, the sulphate/chloride ratio was observed to decrease with depth, approaching zero at all locations except Site 1. This trend and the presence of sulphate/chloride ratios less than 0.140 may be attributed to the loss of sulphate during sulphate reduction in these sediments. Sulphate/chloride ratios greater than 0.140 in these cores were observed only in the surficial sediments of Sites 1 and 5. A number of processes within the sediments may increase this ratio, including: 1) oxidation of sulphate minerals or elemental sulphur, 2) dissolution of sulphate minerals and 3) sulphate ion exchange involving clay minerals. In addition, sulphate/chloride ratios in river water are generally much greater than in seawater (Riley and Chester, 1971). Thus, land runoff may appreciably increase this ratio in estuaries such as Great Bay. However, oxidation of reduced sulphur species (especially FeS or FeS_2), in the sediments is thought to be largely responsible for sulphate/chloride ratios greater than 0.140 (Hines, 1981; and Lyons, personal communication).

The seasonal variability of chloride and sulphate in the pore water of sediments from Site 4 in Great Bay is illustrated in Figure 4-16. In these cores, chloride showed no significant seasonal variation below 15 cm in the sediment; chlorinities averaged about 13.5 °/oo. In the top 15 cm of sediment, a slight increase in chlorinity was observed between the August and October cores (13.5 °/oo to 16.5 °/oo). This

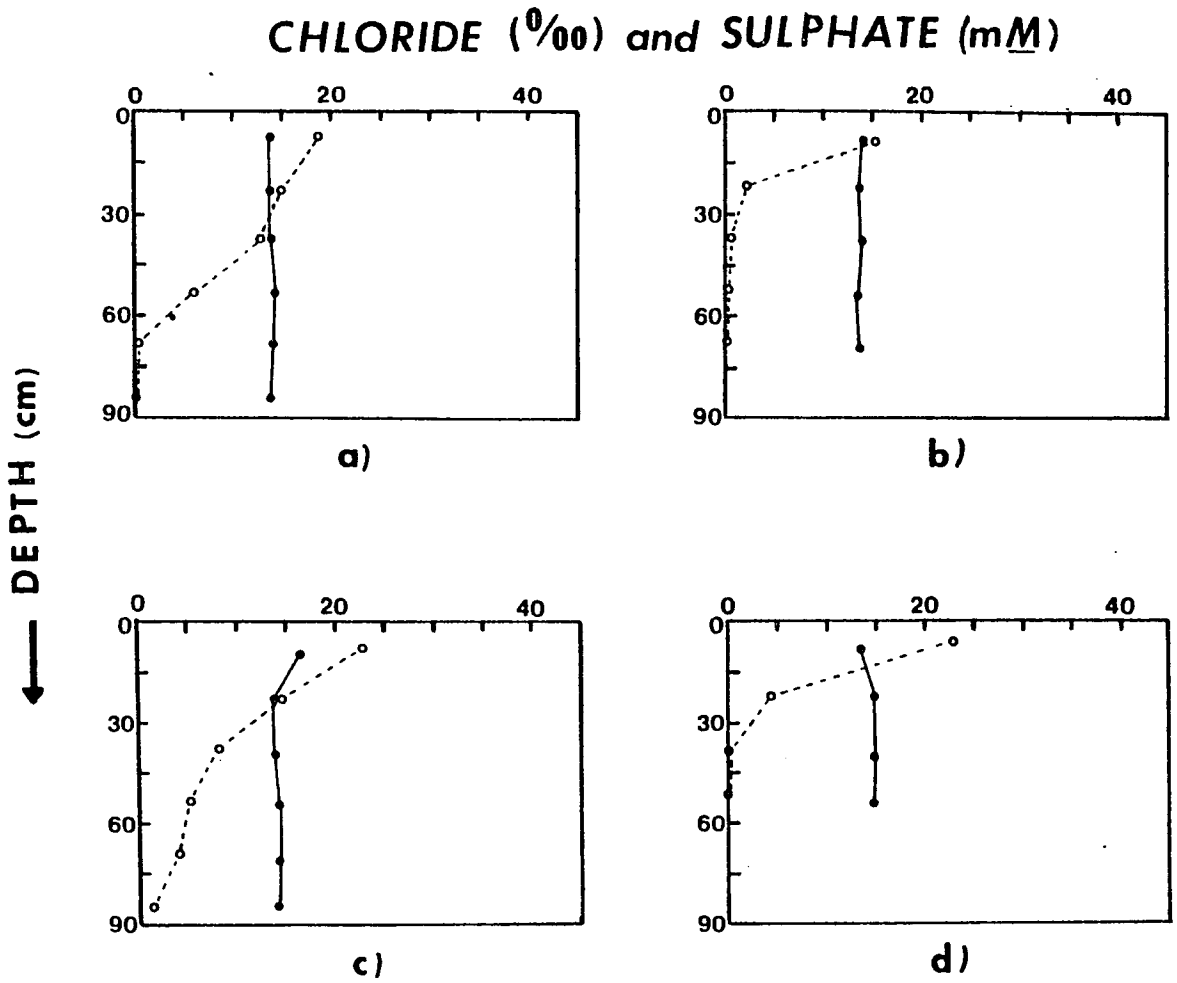

Figure 4-16. The seasonal variation of chloride (‰), (●—●), and sulphate (mM), (o---o), in gravity cores from Site 4 (Footman Islands): a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); c) Core OAX-II (10-21-80); and d) Core UF-IX (4-15-81).

chlorinity then decreased again to 13.5 °/oo in the April core. The small seasonal variability of chloride in the pore water of Great Bay sediments was in marked contrast to that in the overlying seawater, which ranged from 1 °/oo during the spring runoff to 15 °/oo in the summer. This is a dramatic example of the slow diffusion of ions into and out of clastic marine sediments.

In contrast to the chloride results, sulphate concentrations in the cores in Figure 4-16 showed a significant seasonal variation. This was not a surprising result, since sulphate concentrations in anoxic pore water are controlled by biological processes (e.g. bacterial sulphate reduction), which are temperature dependent. In all of these cores, sulphate concentrations were observed to decrease with depth as a consequence of sulphate reduction. In the June core (Figure 4-16a), sulphate concentrations showed a nearly linear decrease with depth from about 18.5 mM in the 0-15 cm section to 0 at about 70 cm. By mid August, the shape of the sulphate depth profile had changed to one of exponential decrease. In addition, the concentration of sulphate had decreased in all depth sections, ranging from about 14.5 mM in the top 15 cm of sediment, to 0 by about 40 cm. The lower sulphate concentrations are a result of increasing microbial sulphate reduction activities over this period (particularly in the upper sediments), such that diffusions of sulphate from the overlying water is insufficient to maintain the previous steady-state concentration. The correlation between seasonal temperature change and bacterial sulphate reduction has been previously shown (Abdollahi and Nedwell, 1979; and Nedwell and Abram, 1979). However, these observed seasonal trends may involve more than a simple temperature dependence, considering the complex interrelation-

ships among the various types of heterotrophic bacteria in anoxic marine sediments. Sulphate concentrations at all depths in the fall core (Figure 4-16c), were significantly higher than those observed in August. In fact, sulphate concentration in this fall core never reached zero, but ranged from about 22.5 mM in the surficial sediments to about 2 mM at a depth of 80 cm. A similar variation in sulphate concentrations between summer and fall cores at Site 4 was observed by Lyons and Gaudette (1979). The higher sulphate concentrations in the fall core are an indication of lower rates of sulphate reduction compared to summer values. The sulphate concentrations observed in April (Figure 4-16d), presented an interesting paradox. In the surface sediments, the concentration of sulphate was exactly the same as that observed in the October core (e.g. 22.5 mM), and significantly higher than the values from the June and August cores. This was expected, considering the lower temperatures and rates of sulphate reduction in April relative to June and August. Below the 0-15 cm sediment section, however, the sulphate profile in the April core was analogous to that observed in August, with the sulphate concentration reaching 0 at a depth of only about 40 cm. This was a puzzling result, considering the low rates of sulphate reduction expected in the early spring. The reasons for the low sulphate concentrations observed in the April core are uncertain, however, it is unlikely that sulphate reduction is involved since no analogous increases in titration alkalinity, ammonia or phosphate (all endproducts of bacterial sulphate reduction), were observed. Sulphate/chloride ratios in these cores were generally less than the value of 0.140 for standard seawater. Only the 0-15 cm sediment section in the April core had a ratio greater than 0.140 (the

observed ratio in this sediment section was 0.160), probably a result of oxidation of reduced sulphur species.

The seasonal variation of chloride and sulphate in box cores from Site 3 (Adams Cove), is illustrated in Figure 4-17. Over the period March through November, chlorinities in these cores were observed to gradually increase from average values to 9.4 °/oo in March to a relatively constant 14 °/oo in July through November. A similar seasonal trend was observed at Site 4, the Footman Islands (see Appendix B). The low chloride values in the pore water during March through May, may be attributed to the lower chlorinities of the overlying water during the spring runoff. In the late spring and early summer, the chlorinities of the overlying seawater begin to rise, and as a result of ionic diffusion so does the chloride concentration of the pore water. Bioturbation may also play a role in the summer cores in maintaining an equilibrium between the chlorinities of the overlying seawater and the pore water.

Whole core average sulphate concentrations in the box cores in Figure 4-17 showed a rather pronounced seasonal variability. In the early spring, average sulphate concentrations were observed to increase from 8.7 m$\underline{M}$ in the March core, to values of 10.7 and 10.8 m$\underline{M}$ in April and early May, respectively. The reasons for this increase is unclear, but it is apparently not a consequence of higher sulphate reduction rates in March (Hines, 1981). It may be that some further oxidation of reduced sulphur species in the sediment was occurring between the March and April cores. Average sulphate values were observed to decrease to 8.15 m$\underline{M}$ in late May and 9.71 m$\underline{M}$ in the June core. This decrease was correlated with increasing rates of sulphate reduction over this same

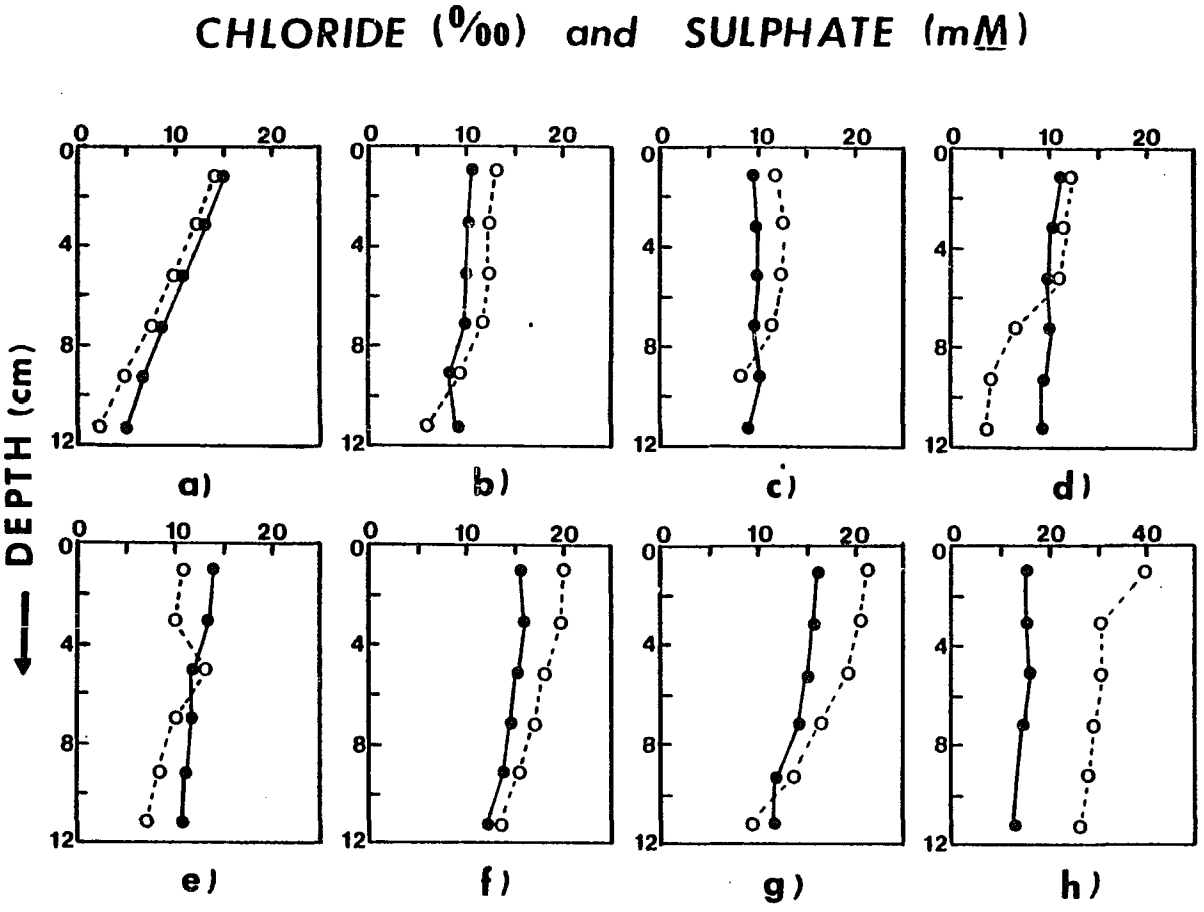

Figure 4-17. The seasonal variation of chloride (°/oo), (●—●), and sulphate (mM), (o---o), in box cores from Site 3 (Adams Cove); a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

period (Hines, 1981). Following the early June core and the onset of bioturbation, average sulphate values showed a sharp increase at this site to values of 17.1 and 16.4 mM in the July and August cores, respectively. This dramatic rise in the sulphate concentration of the pore water was undoubtably a result of advection of overlying seawater into the sediments by bioturbating benthic organisms, since sulphate reduction rates were very high over this period (Hines, 1981). A very high average sulphate concentration of 29.7 mM was observed in the November box core. This was similar to the sulphate concentration observed in the surficial sediments of the October gravity core at Site 4 (see Figure 4-16), and probably resulted from the oxidation of reduced sulphur species in the top 0-15 cm of sediment.

Both chloride and sulphate concentrations in the box cores in Figure 4-17 were observed to decrease with increasing depth. Because of the decreasing chloride depth profiles, sulphate/chloride ratios were calculated to allow interpretation of the effects of sulphate reduction on the observed sulphate concentrations. These results are presented in Figure 4-18. Except for the values in the November box core (Figure 4-18h), the sulphate/chloride ratios were less than that for standard seawater (i.e. 0.140). The probable reason for the high ratios observed in surficial sediments in the fall was discussed earlier. In the early spring cores (Figure 4-18 a, b and c), the sulphate/chloride ratios were relatively constant to a depth of about 7 cm. Average values for these ratios over this depth range were: 0.097 in March, 0.119 in April and 0.117 in early May. Below a depth of 7 cm, a nearly linear decrease in the sulphate/chloride ratio was observed in these cores, as a result of bacterial sulphate reduction. By late May (Figure 4-18d), the sulphate/

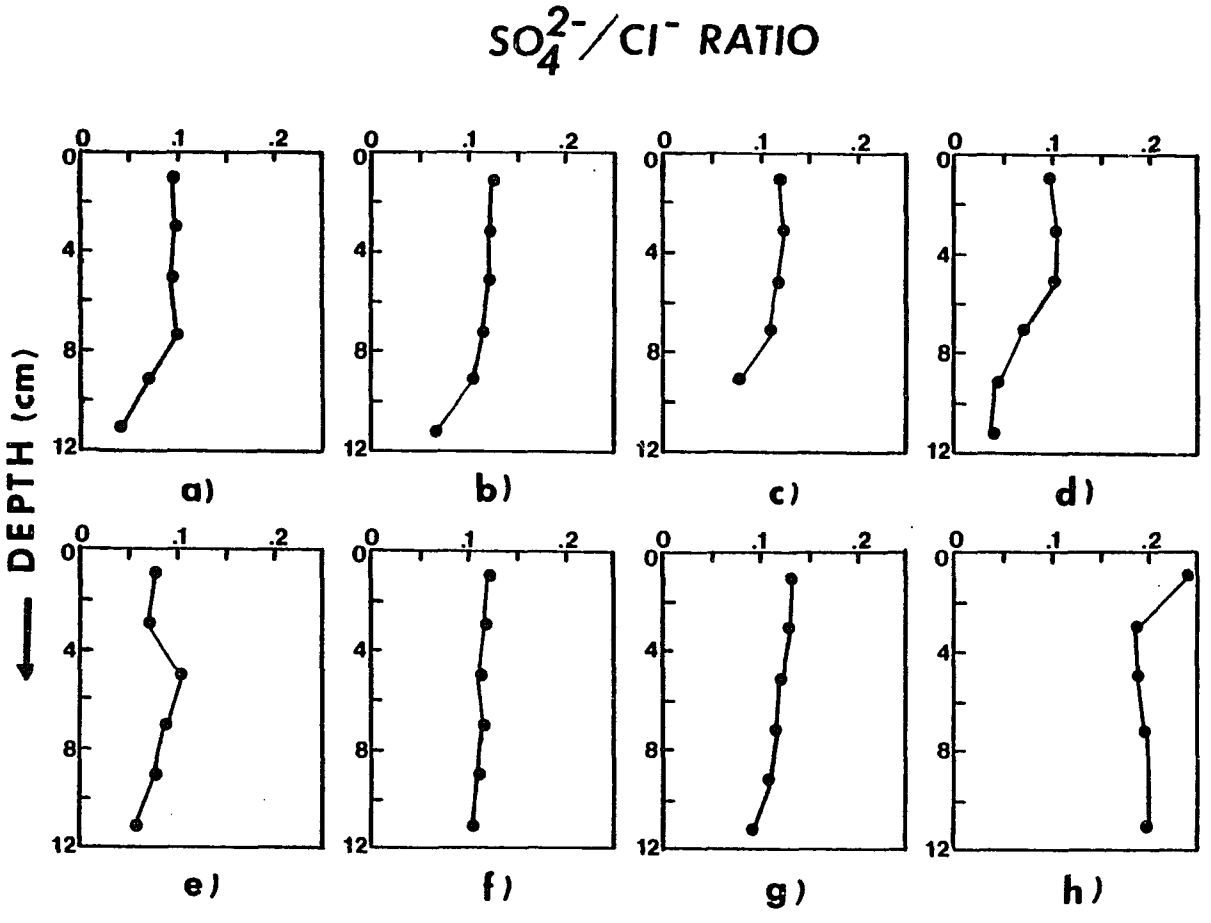

Figure 4-18. Sulphate/chloride ratios for box cores from Site 3 (Adams Cove): a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

chloride ratio showed a decrease below a depth of 5 cm. The upward movement of the sulphate reduction zone is due to the faster rates of sulphate reduction compared to diffusion and advection of sulphate into the sediments. The faster sulphate reduction rates over this period were probably coupled to increasing sediment temperatures. The onset of bioturbation in June resulted in the enhanced transport of overlying seawater into the sediments, and the nearly vertical sulphate/chloride depth profiles observed in July and August (Figures 4-18 f and g, respectively). The June box core (Figure 4-18e), seems to represent a transition between the unbioturbated spring cores and the heavily bioturbated summer cores. The higher whole core average sulphate/chloride ratios in June, July and August (0.0783, 0.114, and 0.112, respectively), relative to the late May value (0.0756), is a vivid example of the effects of bioturbation, since sulphate reduction rates have been observed to be much higher in the summer cores (Hines, 1981).

Nutrients. The pore water of Great Bay anoxic sediments was analyzed for a number of nutrient chemical species, including: nitrate plus nitrite, ammonia and phosphate. These inorganic species are termed nutrients because of their essential role in the growth and production of phytoplankton in the sea (Raymont, 1963). Although this term has little bearing on the cycling of these compounds in marine sediments, they are grouped for discussion under this heading for convenience. The results for nitrate plus nitrite will not be presented here because of questions regarding the accuracy of the data, as discussed in Chapter 2.

Profiles of ammonia and phosphate concentrations versus depth

in gravity cores from the five Great Bay sampling sites are illustrated in Figures 4-19 and 4-20, respectively. All of these cores were obtained during the summer months, the period of highest bacterial activity. In general, ammonia and phosphate concentrations were observed to increase with depth. Similar trends for ammonia and phosphate have been observed by previous workers in the pore water of nearshore marine sediments (Rittenberg et al., 1955; Nissenbaum et al., 1972; Sholkovitz, 1973; Bray, 1973; Berner, 1974; Suess, 1976; and Lyons and Fitzgerald, 1978). These observed trends for ammonia and phosphate in marine sediments result from the heterotrophic bacterial degradation of N and P containing organic matter, and the accumulation of the inorganic by-products of this process (i.e. ammonia and phosphate), in the pore water (Berner, 1980). Although the highest rates of bacterial remineralization of organic matter have been observed in the surface sediments (Hines, 1981), the concentrations of ammonia and phosphate are typically highest in the deepest sediments. A number of factors may account for this apparent discrepancy: 1) diffusional removal fluxes along the concentration gradient are often greatest in the surface sediments, 2) advective removal processes such as bioturbation and wave resuspension are restricted to the surface sediments, 3) deep sediments are somewhat insulated from seasonal temperature changes, and may have significant bacterial activity over longer periods of the year than surface sediments and 4) sediment depth is directly correlated with sediment age and with longer periods for accumulation of ammonia and phosphate in the pore water. The production of ammonia and phosphate from the remineralization of organic matter by bacteria in marine sediments is often represented by the Richards' equation (Richards, 1965):

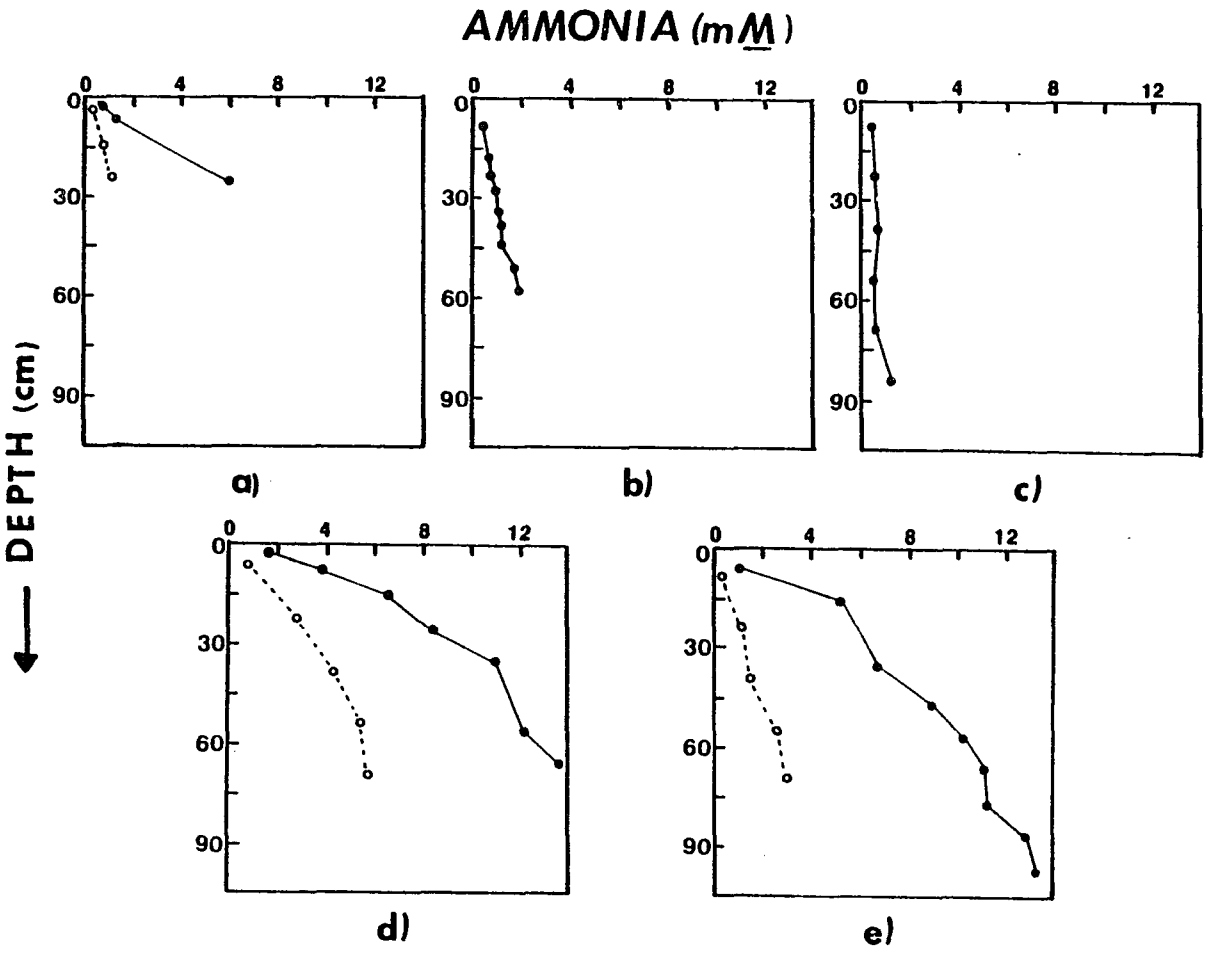

Figure 4-19. Ammonia (mM), versus depth (cm), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River), 7-19-78 (●—●), and 8-11-80 (o---o); b) Site 2 (Welsh Cove), 6-10-78; c) Site 3 (Adams Cove), 7-11-80; d) Site 4 (Footman Islands), 6-30-78 (●—●), and 8-11-80 (o---o); and e) Site 5 (Squamscott River), 8-10-78 (●—●), 7-11-80 (o---o).

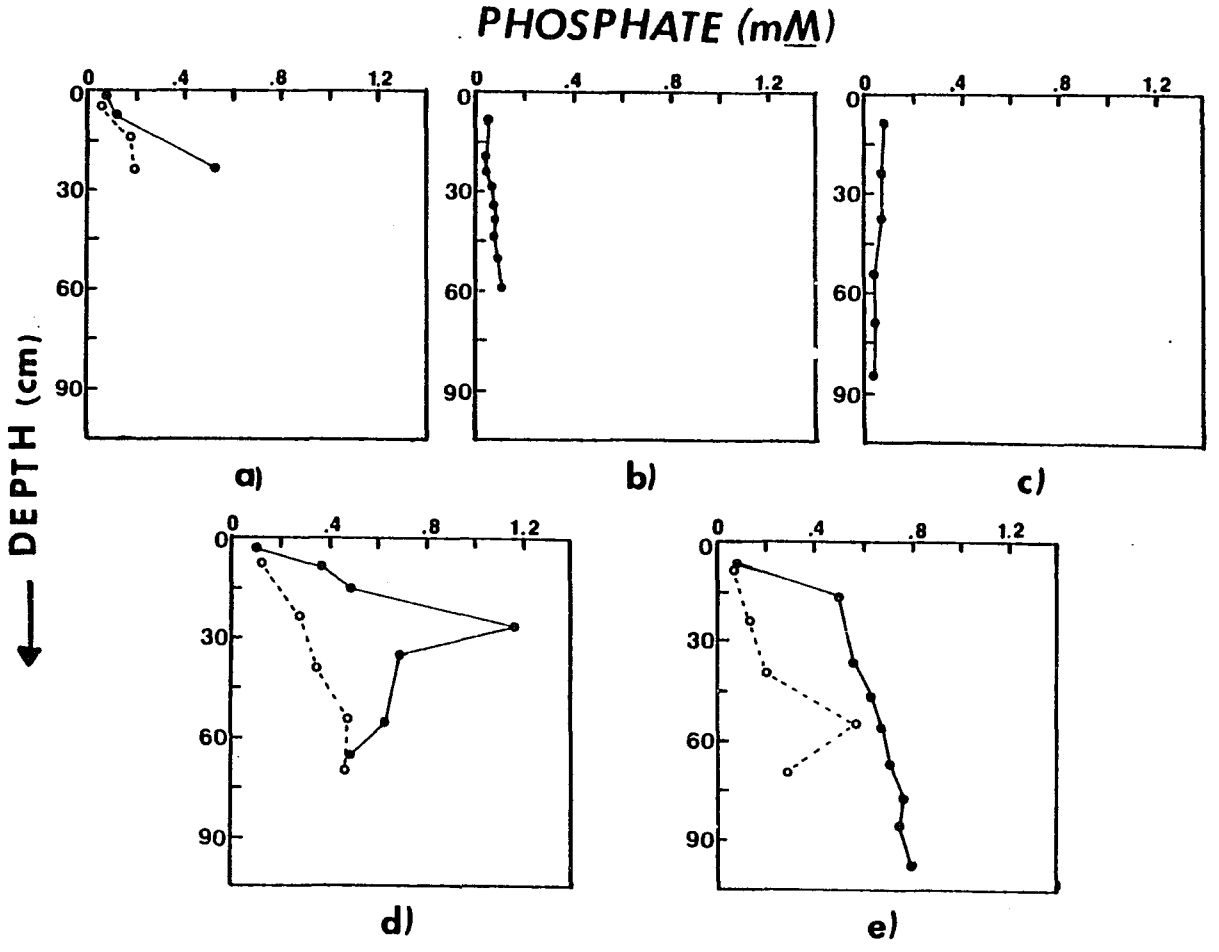

Figure 4-20. Phosphate (mM), versus depth (cm), for the five Great Bay sampling locations: a) Site 1 (Piscataqua River), 7-19-78 (●—●), and 8-11-80 (o---o); b) Site 2 (Welsh Cove), 6-10-78; c) Site 3 (Adams Cove), 7-11-80; d) Site 4 (Footman Islands), 6-30-78 (●—●), and 8-11-80 (o---o); and e) Site 5 (Squamscott River), 8-10-78 (●—●), and 7-11-80 (o---o).

$$(CH_2O)_{106}\ (NH_3)_{16}\ H_3PO_4 + 53\ SO_4^{2-} \longrightarrow 106\ CO_2 +$$

$$53\ S^{2-} + 16\ NH_3 + 106\ H_2O + H_3PO_4,$$

emphasizing the importance of sulphate reducing bacteria (Berner, 1977). Although this equation is useful for modelling this degradation process, it represents an oversimplification of the overall pathway in the remineralization of detrital organic matter in anoxic marine sediments, which involves many different bacterial metabolic processes (Sorokin, 1966; Doelle, 1975; and Hines, 1981).

Ammonia concentrations up to 13mM and phosphate concentrations as high as 1.1 mM were observed in the pore water of these sediments. These values were more than 1000 times those observed for both ammonia and phosphate in the overlying seawater, and represent some of the highest values ever reported for these ions in nearshore marine sediments. Concentrations of ammonia and phosphate were generally higher at Sites 4 and 5 than at Sites 1, 2 and 3. This was similar to the lateral variability observed for titration alkalinity in the estuary. The low phosphate and ammonia values at Site 3 probably resulted from dilution by fresh groundwater influx observed at this location. The low phosphate and ammonia concentrations at Sites 1 and 2 relative to Sites 4 and 5 were undoubtably due to the higher sand and lower organic matter content of the sediments at the former sites.

Two of the phosphate depth profiles in Figure 4-20 showed distinct concentration maxima (e.g. the 6-30-78 core at Site 4 and the 7-11-80 core at Site 5), indicating the possibility of phosphate removal by authigenic mineral formation. These maxima were observed at depths of about 25 cm in the core from Site 4 and about 50 cm in the core from Site 5. The phosphate concentrations reached values of over

1,100 μM at Site 4 and 500 μM at Site 5, before falling to considerably lower values. Similar phosphate depth profiles in nearshore anoxic sediments have been observed by other workers (Bray, 1973; Murray et al., 1978; and Martens et al., 1978). Assuming no sampling or analytical artifacts or reduction of phosphate to phosphine in the sediments, the observed phosphate removal at depth may be accounted for by the formation of a number of authigenic minerals. In carbonate rich sediments, the precipitation of apatite ($Ca_{10}(PO_4)_6(F,OH)_2$), by nucleation on calcite grains or foram tests has been demonstrated (Baturin et al., 1972; Berner, 1974; Manheim et al., 1975; and de Kanel and Morse, 1978). However, in the absence of such nucleation sites (i.e. in most clastic sediments), the precipitation of apatite in marine pore water is inhibited by the presence of Mg^{2+} (Martens and Harriss, 1970). In clastic sediments, indirect evidence (e.g. from calculations and laboratory observations), for the precipitation of struvite ($Mg(NH_4)(PO_4)\cdot 8\ H_2O$), (Bray, 1973; Troup, 1974; and Martens et al., 1978), in marine sediments has been presented.

Calculations similar to those of Martens and co-workers (1978), were carried out using data from the two cores mentioned above to provide indirect evidence regarding the authigenic formation of struvite and vivianite in Great Bay sediments. Details of these calculations have been published (Bray, 1973; Troup, 1974; and Martens et al., 1978). Ion activity products (IAP), for struvite and vivianite were calculated using the following equations:

$$\text{IAP (struvite)} = \gamma_{TMg^{2+}}\ \gamma_{TNH_4^+}\ \gamma_{TPO_4^{3-}} \cdot m_{TMg^{2+}}\ m_{TNH_4^+}\ m_{TPO_4^{3-}}$$

$$\text{IAP (vivianite)} = (\gamma_{TFe^{2+}})^3 \ (\gamma_{TPO_4^{3-}})^2 \cdot (m_{TFe^{2+}})^3 \ (m_{TPO_4^{3-}})^2,$$

where γ is the activity coefficient (Martens et al., 1978), m is the molality and T refers to the sum of free ion plus ion pairs (Kester and Pytkowicz, 1967). The concentration of total magnesium in the pore water was calculated from the chloride concentration and the magnesium/chloride ratio of seawater (Riley and Chester, 1971). This assumes conservative behavior for magnesium in the pore water (Bray, 1973). The calculated IAP's for struvite and vivianite in these two cores are presented in Table 4-2. Equilibrium IAP's or solubility product constants (K_{sp}'s), were obtained from Martens et al., (1978), for struvite ($K_{sp} = 10^{-13.66}$), and from Nriagu (1973), for vivianite ($K_{sp} = 10^{-36.0}$).

A comparison of the calculated IAP values from Table 4-2 to the K_{sp}'s for struvite and vivianite shows that for core PS-II, the pore water is supersaturated with respect to both of these minerals below 5 cm. In contrast, the IAP's for core UF-V indicate that the pore water in these sediments is undersaturated by 2 to 4 orders of magnitude with respect to these mineral phases. Undersaturation with respect to both vivianite and struvite is most commonly encountered in marine sediments, since sufficiently high concentrations of iron, ammonia and phosphate are infrequently attained (Berner, 1980). Core PS-II from Site 4 had unusually high ammonia and phosphate concentrations and moderate iron values, resulting in supersaturation of the pore water with respect to struvite and vivianite, and possibly precipitation of these minerals. The buildup of high ammonia and phosphate values in this core probably resulted from enrichment of the sediments at this site in high-

Table 4-2. Calculated IAP for struvite and vivianite in core PS-II (6-30-78, Site 4); and core UF-V (7-11-80, Site 5). The ammonia and phosphate depth profiles for these cores are illustrated in Figures 4-19 and 4-20, respectively.

Core PS-II
Site 4 (Footman Islands)
Date: 6-30-78

Depth (cm)	log IAP (struvite)	log IAP (vivianite)
0-5	-14.1	-36.7
5-10	-13.1	-35.5
10-20	-12.7	-35.2
20-30	-12.2	-34.5
30-40	-12.3	-34.9
40-50	-	-
50-60	-12.3	-35.0
60-70	-12.4	-35.2

Core UF-V
Site 5 (Squamscott River)
Date: 7-11-80

Depth (cm)	log IAP (struvite)	log IAP (vivianite)
0-15	-16.7	-38.6
15-30	-16.5	-40.0
30-45	-15.7	-39.0
45-60	-15.1	-38.1
60-75	-17.2	-38.3

ly reactive organic matter from an overlying eelgrass bed. Before precipitation of struvite and vivianite can be firmly established as a mechanism for phosphate removal, however, further work is needed, especially on the possible inhibition of authigenic mineral precipitation by dissolved organic matter in pore water. In addition, mineralogical work should be carried out to determine if these mineral phases are actually present in the sediments.

The seasonal variation of ammonia and phosphate in gravity cores from Site 4 (Footman Islands), is illustrated in Figures 4-21 and 4-22. In general, the seasonal trend for ammonia and phosphate was similar to that observed for titration alkalinity, discussed earlier. Between June and August, ammonia and phosphate concentrations were observed to significantly increase in these cores. At a depth of 65 cm, for example, the concentration of ammonia increased by over ten fold and the phosphate concentration by over three fold during this period. Two factors probably account for the higher ammonia and phosphate concentrations in August: 1) increasing bacterial activities (Hines, 1981), and 2) desorption of ammonia and phosphate from sediment grains over this period (Rosenfeld, 1979; Abdollahi and Nedwell, 1979; Nedwell and Abram, 1979; and Krom and Berner, 1980). The desorption phenomenon for ammonia and phosphate probably involves a release of these ions from organic coatings on clay particles (Rosenfeld, 1979; and Krom and Berner, 1980); and may be associated with the seasonal adsorption/desorption of organic carbon observed in Great Bay sediments. The effects of bacterial activity on the observed seasonal trend were probably most pronounced in the surficial sediments. Conversely, the desorption process was likely of more importance in the deeper core sections, where bacterial numbers

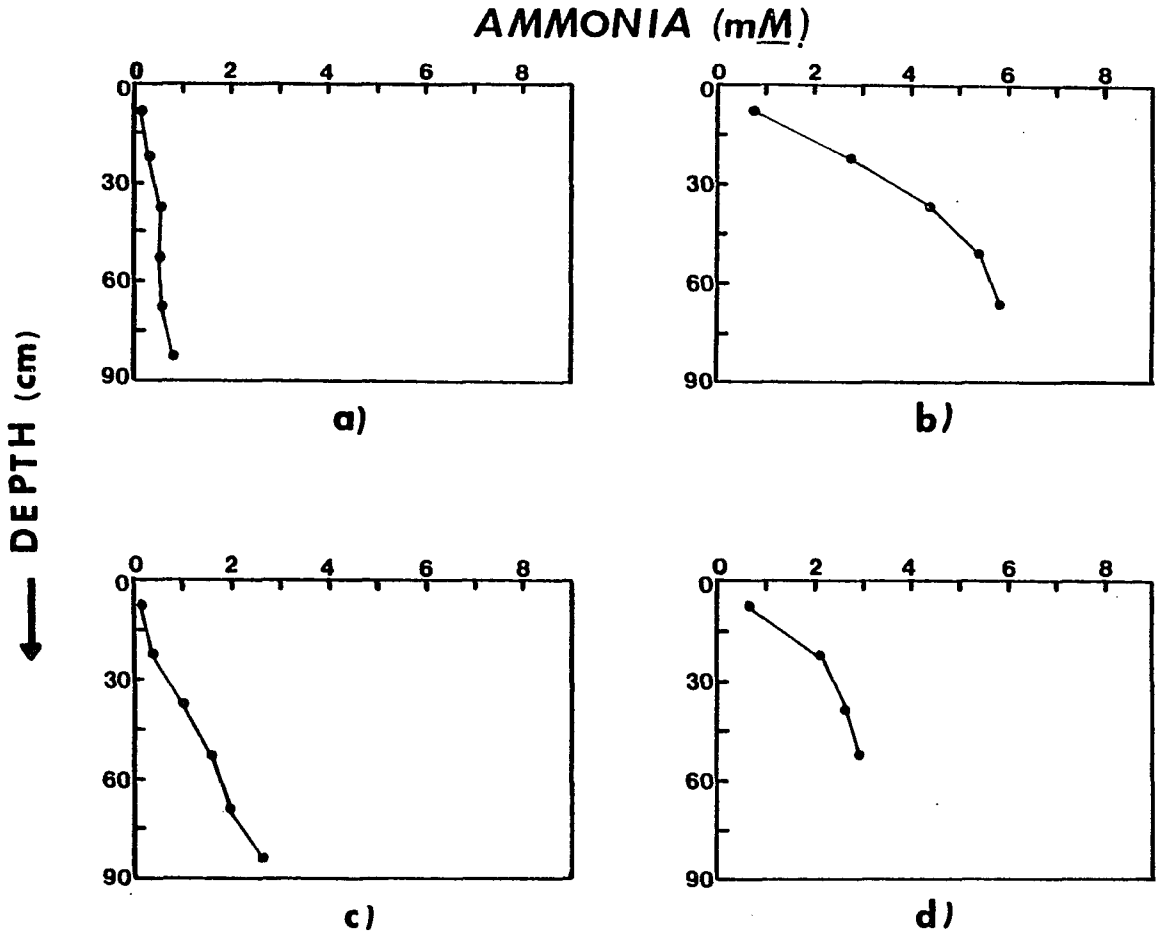

Figure 4-21. The seasonal variation of ammonia (mM), in gravity cores from Site 4 (Footman Islands): a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); c) Core OAX-II (10-21-80); and d) Core UF-IX (4-15-81).

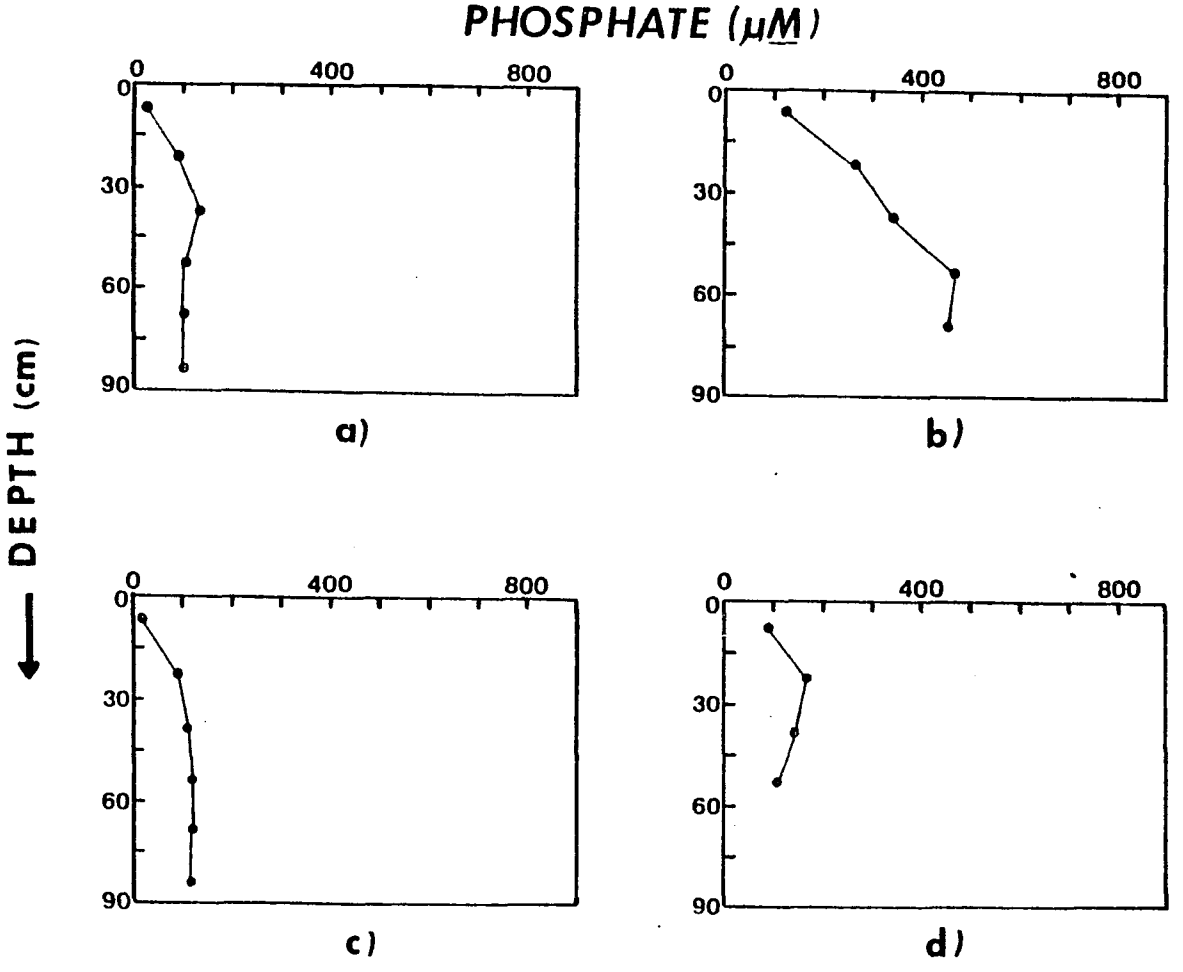

Figure 4-2. The seasonal variation of phosphate (μM), (●—●), in gravity cores from Site 4 (Footman Islands): a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); c) Core OAX-II (10-21-80); and d) Core UF-IX (4-15-81).

and activities are relatively low even during the late summer months (Hines, 1981). Between the August and October cores, concentrations of both ammonia and phosphate decreased sharply. At a depth of 65 cm, both ammonia and phosphate values were observed to be lower by a factor of about three in October relative to August concentrations. The loss of these ions from the pore water at all depths is, again, probably a temperature related process. Cooler temperatures in the sediments during the fall result in lower bacterial metabolic rates. A new equilibrium concentration of these ions in the pore water may then be established by molecular diffusion (and advection in surficial sediments), (Berner, 1980). In addition, these lower temperatures may induce adsorption (or possibly co-precipitation with organic or inorganic colloids), of these ions onto sediment grains, the converse of the desorption process. Moderate increases in both ammonia and phosphate concentrations at all depths were observed between the October and April cores. This result is more difficult to interpret since the surficial sediments were only 2.5^{o}C warmer in April than in October. No temperature data for the deep sediments were available, but it may be that temperatures deep in the cores are actually lower in April (Reeburgh, 1969; and Hines, 1981). However, the results of this study indicate that production of ammonia and phosphate in these cores was enhanced in the early spring, relative to fall values.

The seasonal variation of ammonia and phosphate in box cores from Site 3 (Adams Cove), is illustrated in Figures 4-23 and 4-24. In general, the seasonal trend for these ions closely follows that observed for titration alkalinity, as discussed earlier:

1) A gradual rise in the concentration of these chemical

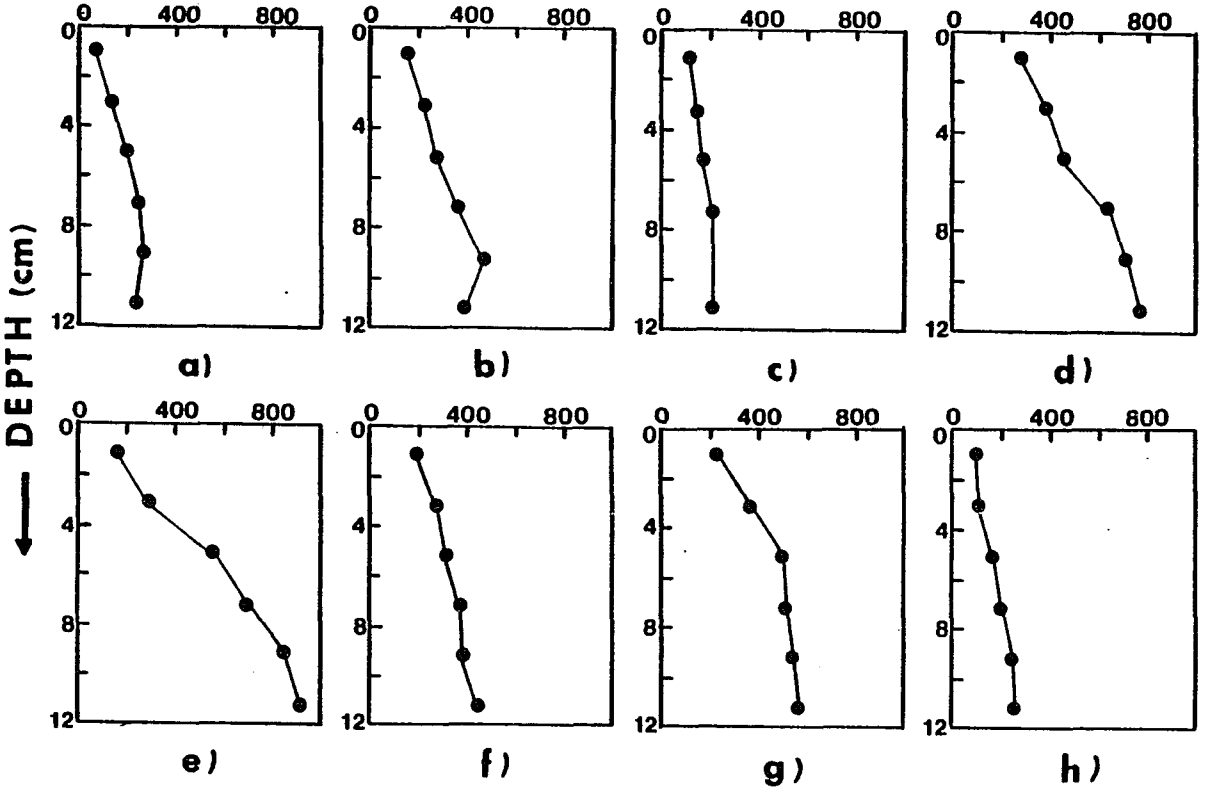

Figure 4-23. The seasonal variation of ammonia (μM), in box cores from Site 3 (Adams Cove): a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

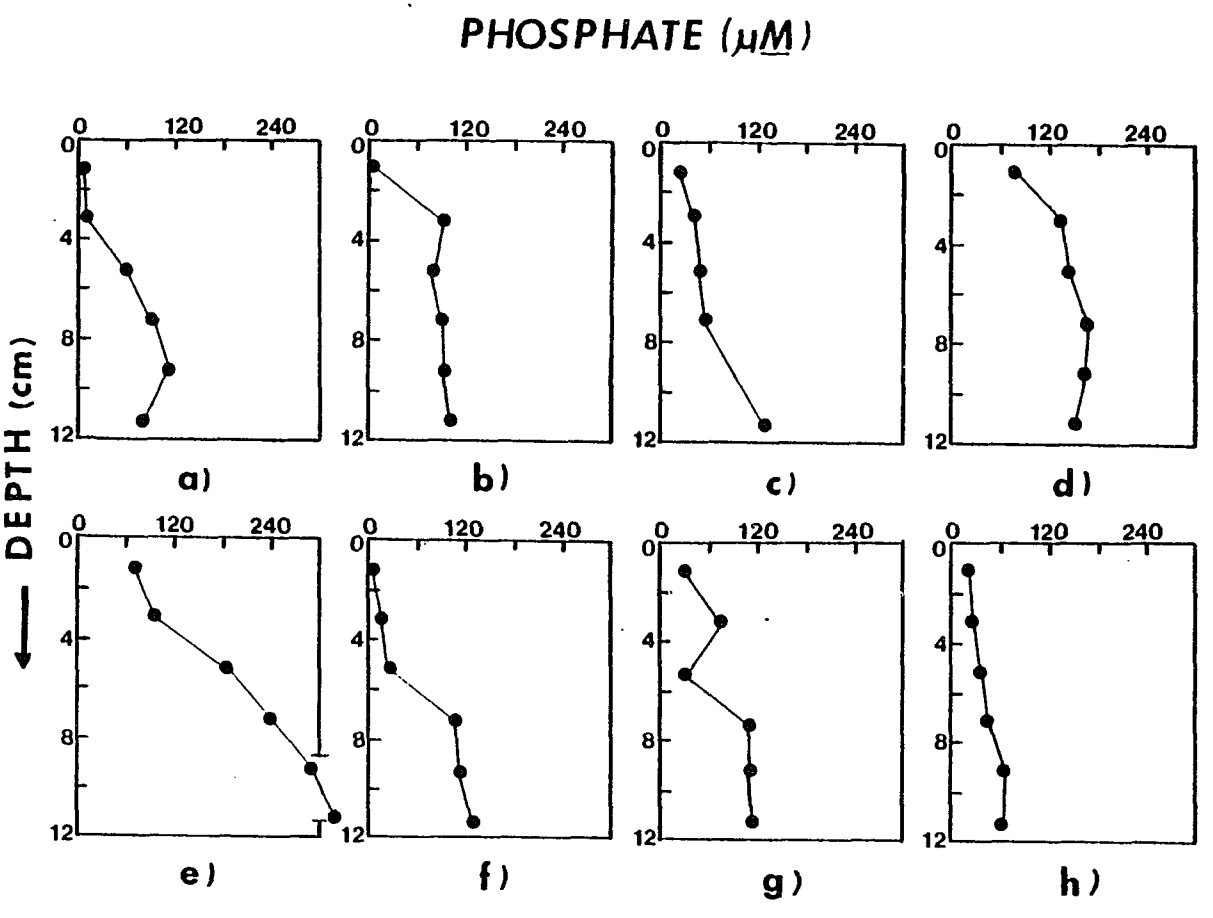

Figure 4-24. The seasonal variation of phosphate (μM), in box cores from Site 3 (Adams Cove): a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

species at all depths through the spring, corresponding to increasing bacterial metabolic rates with rising temperatures over this period.

2) A dramatic reduction in ammonia and phosphate concentrations at all depths after the June core as a result of bioturbation.

3) Low fall and winter concentrations of ammonia and phosphate, correlated with lower temperatures and bacterial activities during this period.

For ammonia, whole core average values were observed to gradually increase from 189 μM in March to 560 μM in June. As a result of bioturbation, the July and August cores had reduced average concentrations of 330 and 437 μM, respectively; despite higher bacterial activities during these months. Cooler fall temperatures and slower bacterial metabolic rates resulted in the low November ammonia concentration of 167 μM. Similarly, whole core average phosphate concentrations varied from 59 μM in March to 194 μM in June, and then showed a dramatic drop in average values to 63 μM in July and 79 μM in August. The November core had an average phosphate concentration of 39 μM. Concentration versus depth profiles for both phosphate and ammonia were similar throughout the year, with values generally increasing as a function of depth.

Total Iron. The concentrations of total dissolved iron in the pore water of Great Bay sediments were determined in a number of box and gravity cores during this study. Total iron refers to the sum of all the dissolved iron species in pore water passing a 0.5 μm filter. Concentrations of total iron versus depth in gravity cores from the five Great Bay sampling sites are illustrated in Figure 4-25. Concentrations were observed to range from 0.2 to nearly 4 ppm in these cores. Verti-

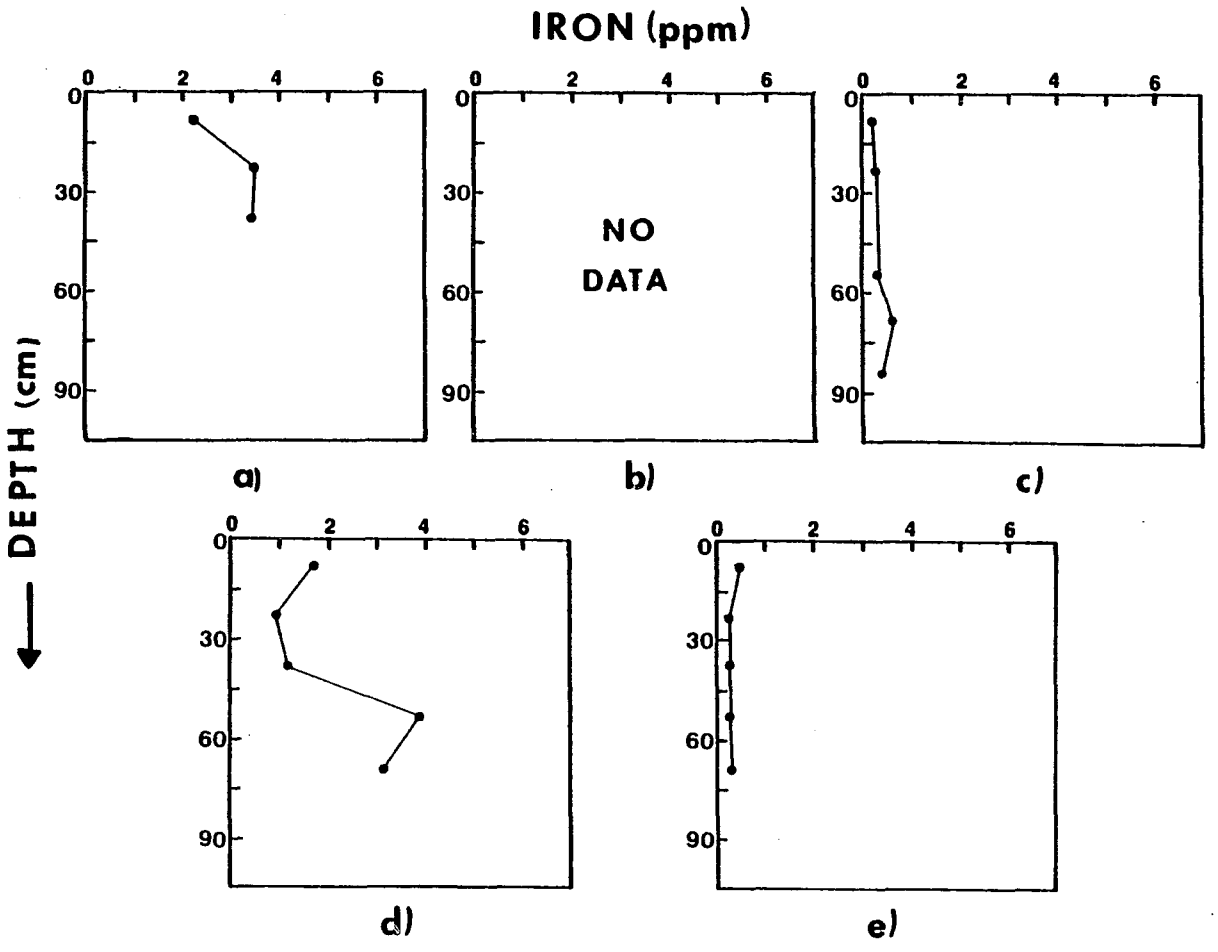

Figure 4-25. Total dissolved iron (ppm), versus depth (cm) for the five Great Bay sampling locations: a) Site 1 (Piscataqua River); b) Site 2 (Welsh Cove); c) Site 3 (Adams Cove); d) Site 4 (Footman Islands); and e) Site 5 (Squamscott River).

cal profiles were somewhat irregular, but seemed to indicate a general trend of increasing concentration with depth at Sites 2, 3 and 4. No data were available for Site 2, and the depth trend at Site 5 was nearly a vertical line. The lateral variability for iron was observed to be quite large, and seemed to follow no easily discernable trend. Whole core average values were 2.9 ppm at Site 1, 0.3 ppm at Site 3, 2.1 ppm at Site 4 and 0.2 ppm at Site 5. Similar depth profiles by other workers in nearshore clastic sediments (Troup, 1974; Matisoff, et al., 1975; Contreras et al., 1978; Murray et al., 1978; Martens et al., 1978; and Lyons et al., 1980). Matisoff et al. (1975), also observed large lateral variability for total iron in Chesapeake Bay pore water, and attributed this to localized equilibria with vivianite. This may also account for some of the lateral variability of dissolved iron in Great Bay sediments. However, the chemistry of iron in anoxic marine sediments is extremely complex, and variations of iron depth profiles and concentrations from core to core are undoubtably the result of a number of interacting factors. These factors include the reduction and dissolution of Fe(III) oxides and hydroxides deposited in the sediments (Berner, 1971), the complexation of Fe(II) in the pore water by dissolved organic matter (Lyons et al., 1979), and the precipitation of dissolved Fe(II) by a number of authigenic iron minerals, such as mackiniwite (FES), pyrite (FeS_2), vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$), and siderite ($FeCO_3$), (Berner, 1967; and Troup, 1974).

No readily discernible seasonal variation for dissolved iron in gravity cores from Site 4 (Footman Islands), was observed (Figure 4-26). In the August, October and April cores, the iron depth profiles were somewhat irregular, with concentrations ranging between 0.9 and 7 ppm.

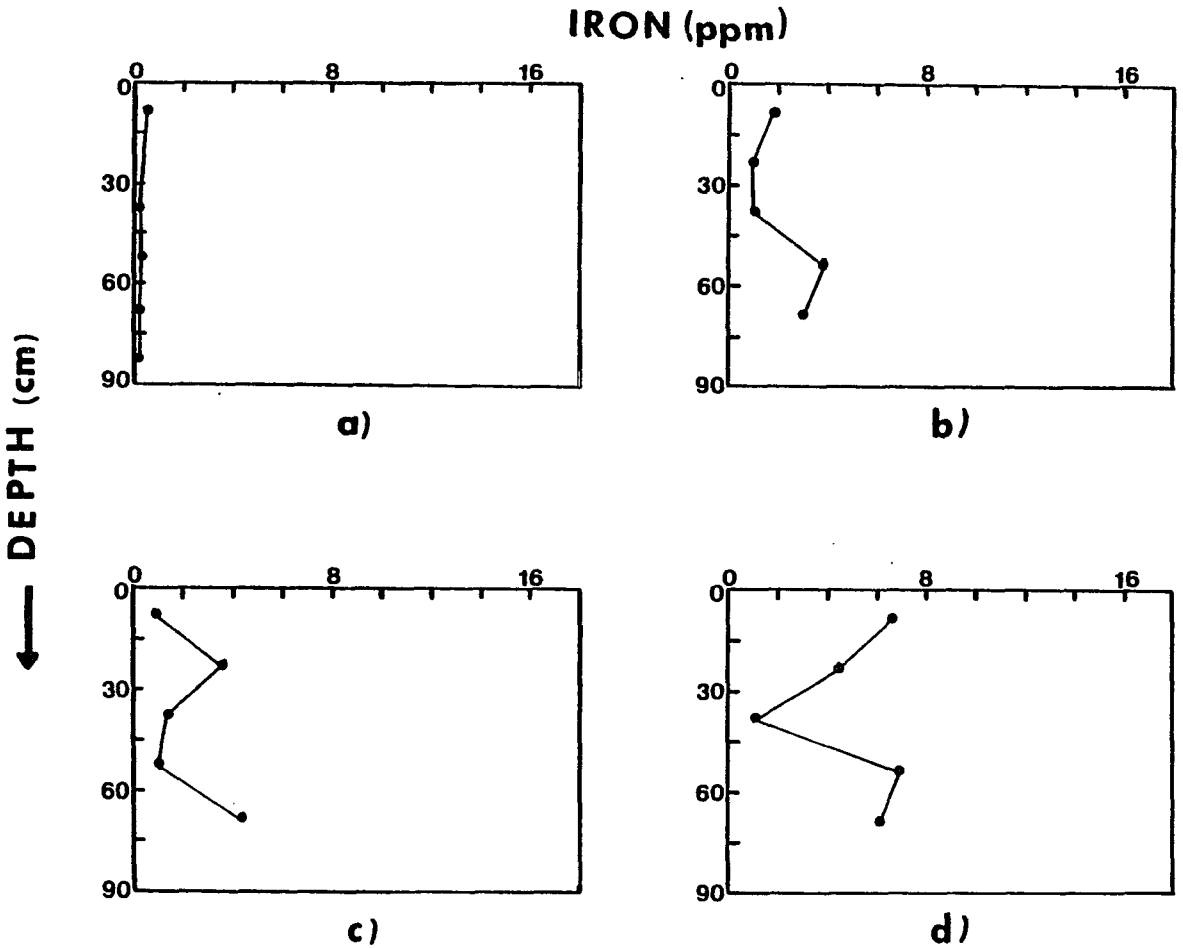

Figure 4-26. The seasonal variation of total iron (ppm), in gravity cores from Site 4 (Footman Islands): a) Core OAX-I (6-23-80); b) Core UF-VII 8-11-80); c) Core OAX-II (10-21-80); and d) Core UF-IX (4-15-81).

Dissolved iron values in the June core were considerably lower, ranging only between 0.1 and 0.3 ppm. Whole core average values steadily increased from the June to the April cores: 0.2 ppm in June, 2.1 ppm in August, 2.3 ppm in October and 5.1 ppm in April. However, the significance of this trend is uncertain, due to the large lateral variability in iron concentrations observed at this sampling location (see Chapter 2). Troup (1974), also was unable to discern any seasonal variation for dissolved iron in gravity cores from Chesapeake Bay sediments, as a result of large spatial variation at a single sampling location. Despite the lack of any quantitative distinction in the dissolved iron concentrations for the August, October and April cores, a certain qualitative similarities for dissolved iron profiles in cores from consecutive monthly cruises. Indeed, the general shape of the iron profiles observed in this study and by Troup (1974), were strikingly similar.

In contrast to the gravity core results, a distinct seasonal variation for dissolved iron in box cores from Site 3 (Adams Cove), was observed (Figure 4-27). The difference between the seasonal results for dissolved iron in gravity cores and box cores is probably attributable to the greater effect of temperature on bacterial activities and, thus, Eh (Hines, 1981), and the greater diffusive and advective fluxes of chemical species from the pore water (Berner, 1980), in surface sediments. All of the box cores in Figure 4-27 had similar vertical profiles, showing decreasing iron concentrations with depth. These profiles probably represent removal of iron from the pore water by authigenic mineral formation. Calculation of ion activity products for vivianite in these cores indicated that the pore waters were generally supersaturated with respect to this mineral. However, it is

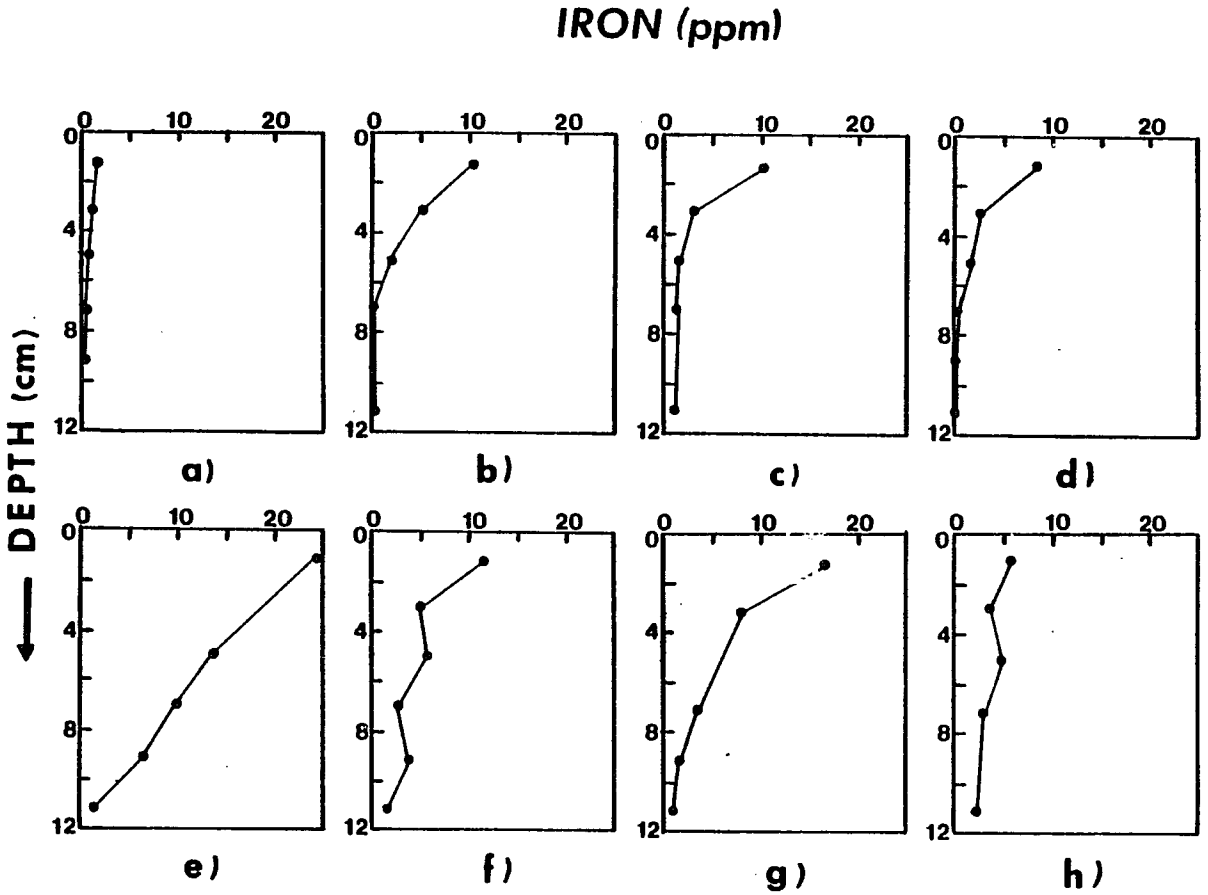

Figure 4-27. The seasonal variation of total iron (ppm), in box cores from Site 3 (Adams Cove): a) 3-10-80; b) 4-9-80; c) 5-2-80; d) 5-20-80; e) 6-2-80; f) 7-2-80; g) 8-1-80; and h) 11-14-80.

likely that the precipitation of iron sulphide minerals (e.g. FeS and FeS_2), is an even more important mode of iron removal (Hines, 1981). Siderite ($FeCO_3$), may also be precipitating (Troup, 1974).

The variation of iron concentrations in these box cores showed a complex interrelationship with three competing factors: 1) increased dissolution of insoluble Fe(III), species with increasing anaerobic bacterial metabolism and concomitant decreasing Eh, through the spring and summer; 2) removal of iron from the pore water by authigenic mineral precipitation, as the byproducts of bacterial sulphate reduction (e.g. sulphide, phosphate and carbonate), accumulate in solution; and 3) removal of iron(III) oxi-hydroxides to the sediments as a result of increased advection of oxygen into the sediments from bioturbation during the summer months. Between the March and April cores, whole core average iron values increased dramatically from 0.64 to 3.40 ppm, as a result of dissolution of insoluble Fe(III) species with decreased Eh over this period. The May 2 and May 20 cores had average iron concentrations of 3.08 and 2.15 ppm, respectively. These values were somewhat lower than the average iron concentration in the April core, probably due to the precipitation of authigenic minerals of iron (e.g. mackiniwite, vivianite and struvite). By the June core, sulphate reduction rates had increased dramatically (Hines, 1981), and this was reflected in the very high average dissolved iron concentration in this core of 10.9 ppm. Average values of dissolved iron in the July and August cores (5.05 and 5.78 ppm, respectively), were considerably diminished compared to the average concentration in the June core. However, these iron concentrations were still relatively high, due to extensive bioturbation at this sampling site. In non-bioturbated sedi-

ments in the Great Bay Estuary (e.g. Site 5), dissolved iron concentrations during the summer months have been observed to approach zero as a result of extensive precipitation of iron authigenic minerals (Hines et al., submitted). Bioturbation, apparently, has a net effect of maintaining relatively high iron concentrations in the pore water during the summer months, despite the increased input of oxygen into the sediments due to bioturbation, and removal or iron(III) oxi-hydroxides. This effect is probably the result of two factors: 1) enhanced advective removal by bioturbation of chemical species in the pore water which induce precipitation of iron (e.g. sulphide and phosphate), and 2) the oxidation of iron sulphides by the transport of oxygen into the sediments during reworking and irrigation by benthic organisms. The November core had an average iron concentration of 3.71 ppm, somewhat lower than the summer values. Cooler temperatures and lower anaerobic bacterial activities during the fall and winter result in increased Eh's, oxidation of dissolved Fe(II) to Fe(III) and the subsequent precipitation of Fe(III) oxides and hydroxides.

In addition to studies of the depth, lateral and seasonal variation of dissolved iron, the molecular size distribution of iron in pore water was also investigated using coarse filtration and ultrafiltration. The results of this work are presented in Table 4-3. Coarse filtration of the pore water for dissolved iron analysis was accomplished using two different filters: Nuclepore^{R} filters with a nominal pore size of 0.5 μm, and Whatman^{R} GF/C filters with a nominal pore size of about 1 μm. The results of this coarse filtration for two gravity cores from Site 4 (Footman Islands), emphasize the relatively large molecular size of the iron in anoxic marine pore water. Pore

Table 4-3. Total iron molecular size distribution.

A. Coarse Filtration

Core OAX-I
Site 4 (Footman Islands)
Date: 6-23-80

Depth (cm)	Total Fe < 1 μm (ppm)	Total Fe < 0.5 μm (ppm)	Δ (ppm)
0-15	0.65	0.24	0.41
15-30	0.64	-	-
30-45	0.66	0.15	0.52
45-60	0.83	0.27	0.55
60-75	0.54	0.17	0.37
75-90	2.10	0.12	1.98

Core CMP-I
Site 4 (Footman Islands)
Date: 6-23-80

Depth (cm)	Total Fe < 1 μm (ppm)	Total Fe < 0.5 μm (ppm)	Δ (ppm)
0-15	0.89	0.37	0.52
15-30	3.01	0.24	2.77
30-45	1.33	0.20	1.13
45-60	0.97	0.20	0.77
60-75	2.09	0.17	1.92
75-90	1.37	0.21	1.16

Table 4-3. continued.

B. Ultrafiltration

Core SQ-10
Site 5 (Squamscott River)
Date: 7-23-79

Depth (cm)	Total Fe (ppm)	Fe <50,000 MW (ppm)	%	Fe <1,000 MW (ppm)	%
0-2	7.73	5.59	72	4.37	56
2-4	2.84	0.36	13	-	-
4-6	4.12	0.16	4	0.12	3
6-8	1.06	0.27	25	0.12	11
8-10	2.27	0.22	10	0.14	6
10-12	1.05	0.39	37	0.10	10

Core JEL XI
Site 3 (Adams Cove)
Date: 4-2-79

Depth (cm)	Total Fe (ppm)	Fe <50,000 MW (ppm)	%	Fe <1,000 MW (ppm)	%
0-2	3.73	1.88	50	-	-
2-4	2.65	-	-	0.27	10
4-6	0.41	0.23	56	0.14	34
6-8	0.21	0.21	100	-	-
8-10	0.22	-	-	-	-
10-12	2.64	0.54	20	-	-

Core OAX-B
Site 3 (Adams Cove)
Date: 6-12-80

Depth (cm)	Total Fe (ppm)	Fe <50,000 MW (ppm)	%	Fe <1,000 MW (ppm)	%
0-3	2.13	0.07	3	-	-
3-6	0.54	0.08	15	.04	7
6-9	0.16	0.07	44	-	-
9-12	0.12	0.02	17	0	0
12-15	0.12	-	-	0	0

water passing the 1 μm filter contains, on average, seven times as much iron as that passing the 0.5 μm filter in these cores. Previous workers have generally used 0.5 μm filtration in the analysis of iron in anoxic marine pore water (Contreras et al., 1978; Martens and Goldhaber, 1978; Martens et al., 1978; Lyons et al., 1979a; and Lyons et al., 1980). The choice of a cutoff material (or in this context from sedimentary material), is arbitrary, with little relationship to the true physicochemical state of the chemical species in question. Traditionally, 0.5 μm filters have been used to differentiate 'dissolved' and 'particulate' material (Goldberg et al., 1952). However, as the results of this study show, much of the iron retained by a 0.5 μm filter is not truely associated with sediment grains, but represent colloidal material in the pore water (Vold and Vold, 1966). The nature of the colloidal iron in anoxic pore water is uncertain, but this material may include flocs of amorphous iron authigenic minerals, iron adsorbed or occluded to organic or inorganic colloids or iron complexed to large organic molecules. Further work is needed to characterize this potentially important pool of 'dissolved' iron.

The results of ultrafiltration experiments on iron in pore water from three box cores obtained from Sites 3 and 5 (Adams Cove and Squamscott River), in Great Bay are also presented in Table 4-3. After filtration through 0.5 μm Nuclepore^{R} filters, the pore water from these cores was ultrafiltered through 50,000 and 1,000 nominal molecular weight cutoff Amicon Diaflo^{R} membranes. The procedure employed for ultrafiltration was discussed in Chapter 2. The results of this study, again, emphasize the importance of colloidal iron in anoxic marine pore water. On average in these cores, 67% of the iron in the pore water

(e.g. the iron passing a 0.5 μm filter), had a nomial molecular weight greater than 50,000. Percentages of 'dissolved' iron greater than 50,000 MW ranged from 0% to 97%. Of the 33% (average), of the 'dissolved' iron less than 50,000 MW, an average of only 5% (14% of the total 'dissolved' iron), was able to pass a 1,000 MW ultrafiltration membrane. However, the percentages of iron less than 1,000 MW had a considerable range of values in these cores (see Table 4-4). Again, the nature of this high molecular weight iron in the pore water is uncertain. However, it is interesting to note two factors: 1) Lyons et al. (1979a) have noted that as much as 30% of the iron in pore water from Great Bay sediments may be organically associated and 2) studies of the molecular weight distribution of dissolved organic carbon in Great Bay sediments from this work (see Chapter 5), indicate that a significant portion of the organic matter 'dissolved' in pore water has a molecular weight greater than 50,000. Furthermore, the complexation of iron by high molecular weight dissolved organic matter formed by the bacterial degradation of algae has been demonstrated in the laboratory (Akiyama, 1973). These results suggest that at least a portion of the colloidal iron in anoxic marine pore water may be bound to high molecular weight dissolved organic matter.

C. Diagenetic Modelling

Berner (1980), has pointed out that the subject of sedimentary diagenesis has been approached on three levels: 1) qualitative generalizations based on depth trends, 2) qualitative predictions based on thermodynamic calculations and laboratory experiments and 3) quantitative descriptions and predictions based on the measurement of reaction rates and the relationship of these measured rates to theoretical rate

expressions. The first two levels mentioned have been dealt with in some detail above, while the third level, described here as diagenetic modelling, is the subject of this section.

The purpose of diagenetic modelling is to describe more precisely the processes that are occurring during the early stages of organic matter degradation in sediments, especially nearshore anoxic marine sediments. This would include the determination of such processes as the speed of sulphate reduction at various depths in the sediment column and the rate of organic matter decomposition.

Two types of diagenetic modelling have been used in the study of nearshore marine sediments: kinetic and stoichiometric. In both cases, pore water depth profiles of various inorganic species are used to predict changes in sediment chemistry. The advantages of studies of pore water chemistry relative to work on the solid sediments were elaborated earlier (see Chapter 1). Stoichiometric models allow the prediction of the composition of the decomposing or metabolizable organic matter based on the relationships among pore water sulphate, ammonia and phosphate depth profiles. A number of workers have used this approach in studies of nearshore marine sediments (Sholkovitz, 1973; Berner, 1977 and 1980; Martens et al., 1978; and Rosenfeld, 1981). The use of simple stoichiometric models requires that plots of dissolved ammonia versus sulphate and of phosphate versus sulphate be straight lines (Berner, 1977). Such linear relationships imply an overall stoichiometric decomposition reaction for sedimentary organic matter. Unfortunately, plots of ammonia and phosphate versus sulphate for Great Bay pore waters are not linear. Thus simple stoichiometric models are not appropriate for use here, and more complex kinetic models will be

applied.

In kinetic models, pore water profiles are described by equations which invoke a steady state balance among ionic diffusion, advection, adsorption and biological activity. This approach has been used successfully by a number of workers to predict the rates of sulphate reduction and ammonia and phosphate production in marine sediments (Berner, 1974 and 1980; Goldhaber et al., 1977; Vanderborght et al., 1977; Murray et al., 1978; and Rosenfeld, 1981). In this section, kinetic models will be applied to pore water results for sulphate, ammonia and phosphate in three cores from Great Bay, New Hampshire.

If steady state diagenesis is assumed, the concentrations of sulphate, ammonia and phosphate in the pore water may be described, respectively, by the following equations:

$$1)\quad D_S \frac{\partial^2 C_S}{\partial X^2} - \omega \frac{\partial C_S}{\partial X} - LFk_S G = 0$$

$$2)\quad \frac{D_N}{1+K_N} \cdot \frac{\partial^2 C_N}{\partial X^2} - \omega \frac{\partial C_N}{\partial X} + \frac{Fk_N N}{1+K_N} = 0$$

$$3)\quad \frac{D_P}{1+K_P} \cdot \frac{\partial^2 C_P}{\partial X^2} - \omega \frac{\partial C_P}{\partial X} + \frac{Fk_P P}{1+K_P} - \frac{K_m\,(C_P - C_{P,\,eq})}{1+K_P} = 0$$

where: C = concentration of dissolved sulphate (C_S), ammonia (C_N), and phosphate (C_P), in mM;

X = depth in the sediments in cm;

G, N and P = Concentrations of metabolizable organic carbon, nitrogen and phosphorus, respectively, in the sediments utilized by sulphate reduction in mmoles/g;

D_S, D_N and D_P = diffusion coefficients for sulphate, ammonia and phosphate, respectively in cm^2/sec;

ω = the net sedimentation rate in cm/sec;

L = stoiciometric constant, relating moles sulphate reduced per mole organic carbon oxidized (normally = ½);

F = porosity of sediment in g/cm^3;

k_S, k_N and k_P = rate constants for sulphate reduction and ammonia and phosphate production, respectively, in units of sec^{-1};

K_N and K_P = adsorption coefficients for ammonia and phosphate, respectively, (unitless);

K_m = constant for authigenic mineral precipitation, (unitless);

Berner (1980). In addition, the concentrations of metabolizable organic carbon (G), nitrogen (N), and phosphorus (P), in the sediments utilized by sulphate reduction under steady state conditions may be represented, respectively, by the following equations:

$$4) \quad -\omega\frac{\partial G}{\partial X} - K_S G = 0;$$

$$5) \quad -\omega\frac{\partial N}{\partial X} - K_N N = 0;$$

$$6) \quad -\omega\frac{\partial P}{\partial X} - K_P P = 0;$$

(Berner, 1980).

The solutions for these various equations under the boundry conditions described by Berner (1980), are listed in Table 4-4. The equations for sulphate, ammonia and phosphate have been fitted to concentration versus depth profiles for these ions in three cores from Great Bay. These plots are presented in Figures 4-28, 4-29 and 4-30. Using these solutions and the coefficients from the fitted equations for sulphate, ammonia and phosphate, rate constants for the production of ammonia and phosphate and for sulphate reduction were calculated, assuming sedimentation rates of 0.21 cm/yr. at Site 4 and 0.24 cm/yr. at Site 5 (Leavitt, 1979). These rate constants are presented in Table 4-5, and are similar to values observed by other workers in nearshore

Table 4-4. Solutions to steady state diagenetic equations for sulphate, ammonia and phosphate and metabolizable organic carbon, nitrogen and phosphorus.

Sulphate and Organic Carbon:

$$C_S(X) = \frac{\omega^2 F L G_o}{\omega^2 + k_S D_S} \exp((-k_S/\omega)X) + C_S(\infty)$$

$$G = G_o \exp(-(k_S/\omega)X)$$

Ammonia and Organic Nitrogen:

$$C_N(X) = \frac{\omega^2 F N_o}{D_N k_N + (1+K_N)\omega^2} (1-\exp((-k_N/\omega)X) + C_N(0)$$

$$N = N_o \exp((-k_N/\omega)X)$$

Phosphate and Organic Phosphorus:

$$C_P(X) = \frac{\omega^2 F P_o}{D_P k_P + (1+K_P)\omega^2} (1-\exp(-k_P/\omega)X) + C_P(0)$$

$$P = P_o \exp((-k_P/\omega)X)$$

where:

G_o, N_o and P_o represent the amounts of metabolizable organic carbon, nitrogen and phosphorus, respectively, at the sediment/water interface in mmoles/g.

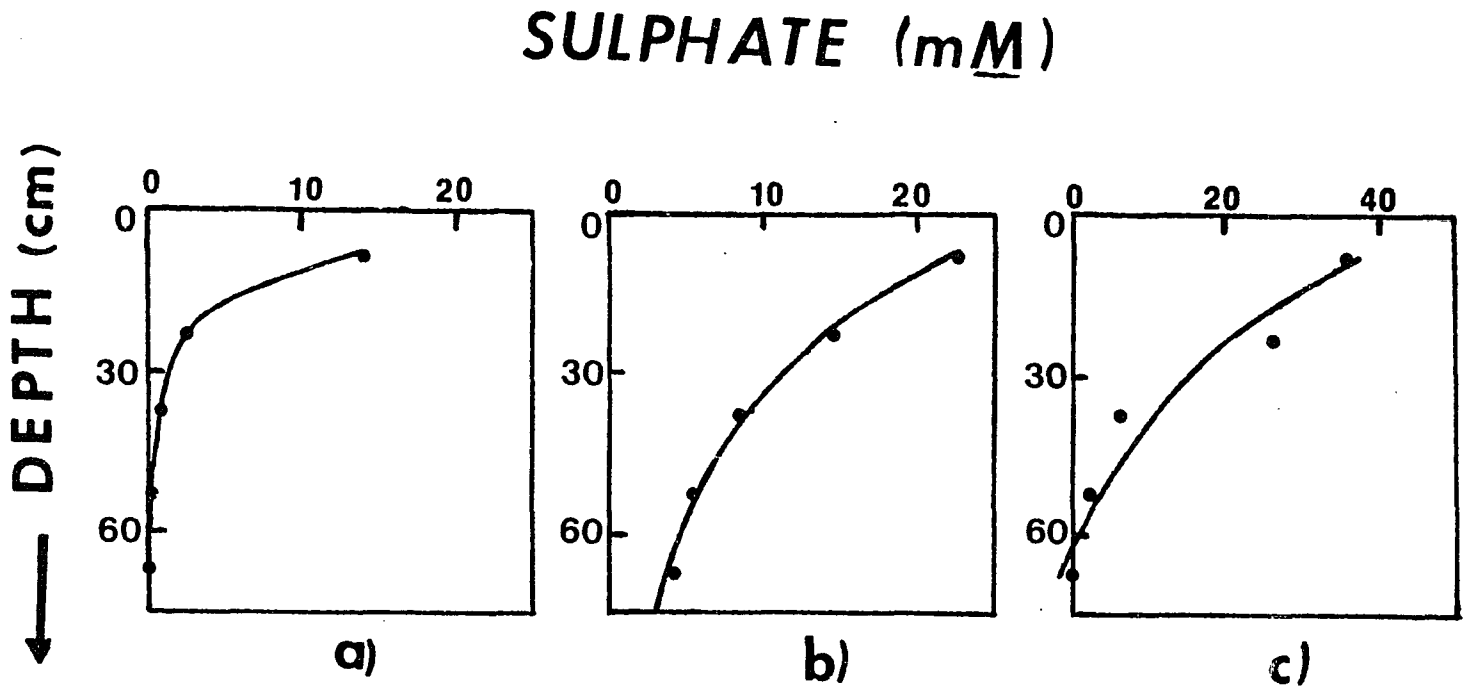

Figure 4-28. Fitted exponential curves for dissolved sulphate (mM), versus depth (cm), for three Great Bay cores: a) Site 4 (8-11-80); b) Site 4 (10-21-80); and c) Site 5 (7-11-80). The fitted equations are: a) C = 33.9 (EXP(-0.120x)) + 0.0643; b) C = 27.9 (EXP(-0.0352x)) + 1.27; and c) C = 59.1 (EXP(-0.0268x)) - 11.3.

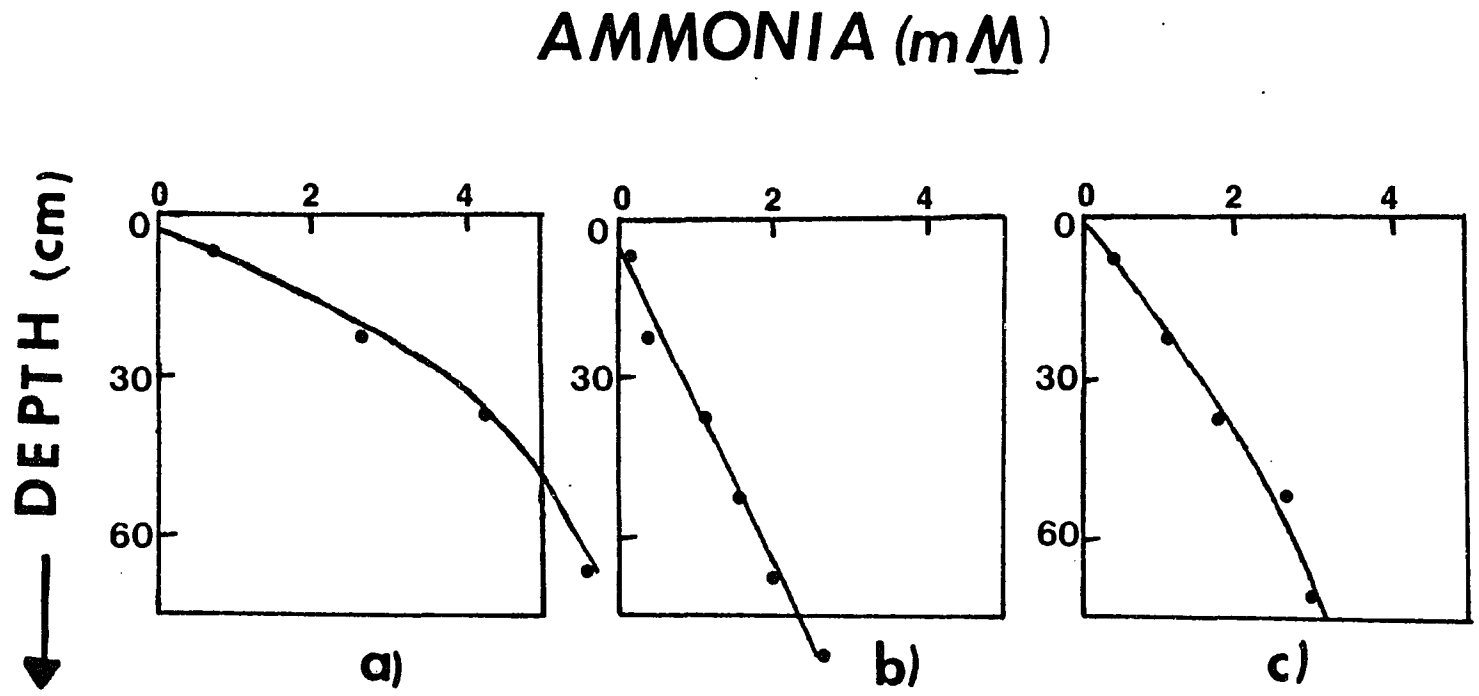

Figure 4-29. Fitted exponential curves for dissolved ammonia (mM), versus depth (cm), for three Great Bay cores: a) Site 4 (8-11-80); b) Site 4 (10-21-80); and c) Site 5 (7-11-80). The fitted equations are: a) C = 7.65 (1-EXP(-0.0277x)) - 0.766; b) C = 251 (1-EXP(-0.000134x)) - 0.213; and c) C = 8.75 (1-EXP (-0.00644x)) - 0.0728.

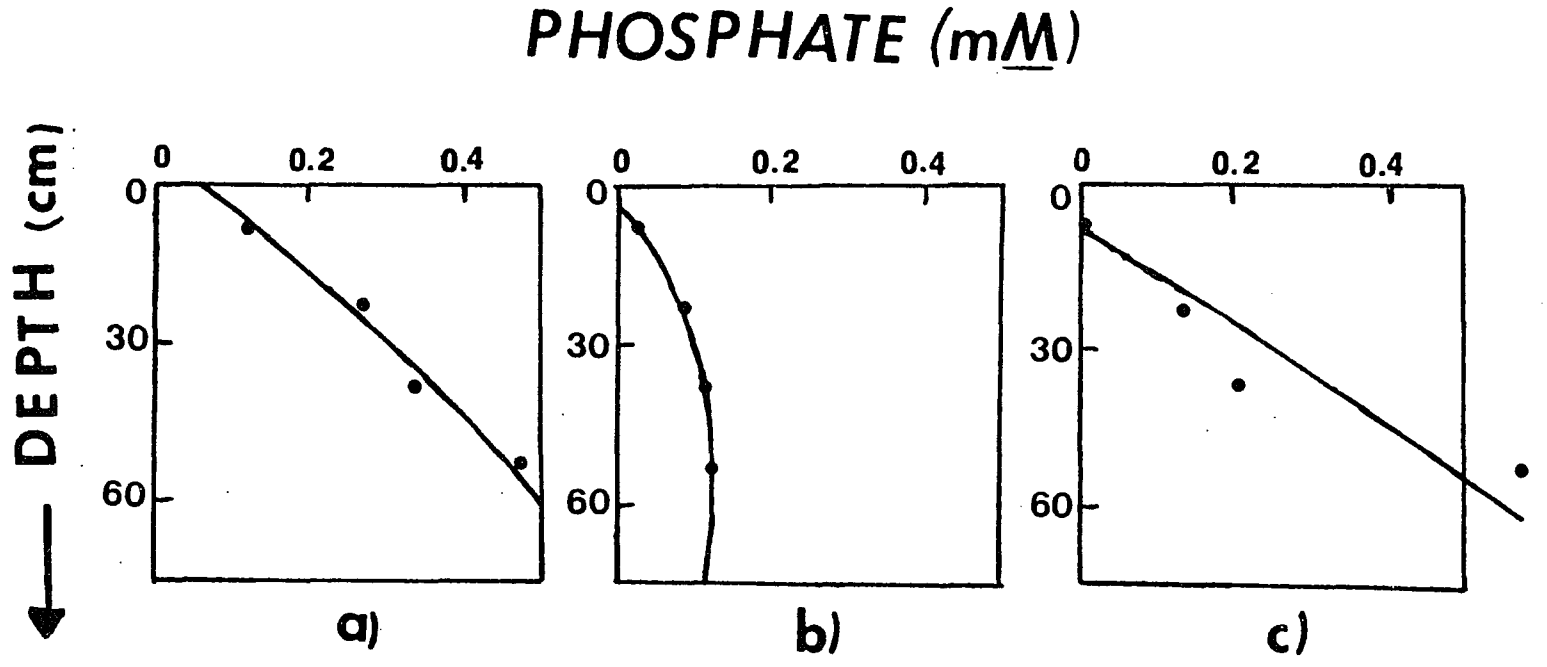

Figure 4-30. Fitted exponential curves for dissolved phosphate (mM), versus depth (cm), for three Great Bay cores: a) Site 4 (8-11-80); b) Site 4 (10-21-80); c) Site 5 (7-11-80). The fitted equations are: a) C = 1.57 (1-EXP(-0.0058 x)) + 0.0650; b) C = 0.171 (1-EXP(-0.0677x)) - 0.0459; and c) C = 145 (1-EXP (-0.0000726x)) - 0.0708.

Table 4-5. Rate constants for sulphate reduction and ammonia and phosphate production, and the predicted amounts of metabolizable organic carbon, nitrogen and phosphorus in the surface sediments for two cores from Site 4 (Footman Islands), and a core from Site 5 (Squamscott River).

Location	Rate Constants (sec^{-1}) k_S	k_N	k_P
Site 4 (August)	8.0×10^{-10}	1.9×10^{-10}	3.7×10^{-11}
Site 4 (October)	2.3×10^{-10}	8.9×10^{-13}	4.5×10^{-10}
Site 5 (July)	2.7×10^{-10}	4.9×10^{-11}	5.5×10^{-13}

Location	Amounts of Metabolizable Organic C, N and P (%)[a] G_o	N_o	P_o
Site 4 (August)	9.3	0.57	0.037
Site 4 (October)	2.3	1.1	0.026
Site 5 (July)	4.3	0.16	1.7

a) Reported as a weight percentage of the sediment.

marine sediments (Berner, 1974 and 1980; and Lyons and Fitzgerald, 1978). It is interesting to note the generally lower rate constants for sulphate, ammonia and phosphate at Site 5 compared to those for Site 4 at the same time of year (i.e. summer). This may be indicative of the greater metabolizability of the organic matter at Site 4 compared to Site 5, and is consistent with the proximity of Site 5 to terrestrial runoff and the presence of an eelgrass bed at Site 4.

A seasonal variation in these rate constants was observed at Site 4, with lower rates of sulphate reduction and ammonia production in October relative to August. However, the rate of phosphate production in the October core was more than an order of magnitude greater than that observed in August. In addition, the rate constant for phosphate production at Site 4 in October was greater than those for sulphate consumption and ammonia production. This may suggest that the rate of phosphate production is not completely coupled to organic matter degradation in the fall, and may reflect the formation of phosphate in the pore water by the dissolution of phosphate minerals (Lyons and Fitzgerald, 1978).

Values of G_o, N_o and P_o (e.g. the amounts of metabolizable organic carbon, nitrogen and phosphorus, respectively, in the surface sediments), may be calculated using the following relationships and coefficients from the fitted equations in Figures 4-28, 4-29 and 4-30:

$$C_S(0) - C_S(\infty) = \frac{\omega^2 \, F \, L \, G_o}{\omega^2 + k_S \, D_S} \quad ;$$

$$C_N(\infty) - C_N(0) = \frac{\omega^2 \, F \, N_o}{\omega^2 \, (1+K_N) + D_N \, k_N} \quad ;$$

$$C_P(\infty) - C_P(0) = \frac{\omega^2 \, F \, P_o}{\omega^2 \, (1+K_P) + D_P \, k_P} \quad ;$$

where the various symbols have the same meanings as listed above. Substituting in the values: ω = 0.21 cm/yr. (Site 4), or 0.24 cm/yr. (Site 5); F = 0.8 g/cm^3 (Berner, 1980); L = 0.5 (Berner, 1980); D_S, D_N and D_p = 5 x 10^{-6}, 9.8 x 10^{-6} and 3.6 x 10^{-6} cm^2/sec, respectively (Krom and Berner, 1980); K_N and K_p = 1.3 and 2.0, respectively (Berner, 1980); and the values of k_s, k_N and k_p from Table 4-5; concentrations of G_o, N_o and P_o were obtained. These values are also presented in Table 4-5.

Measured values for total sedimentary organic carbon, nitrogen and phosphorus in the top 15 cm of sediment at Site 4 were 2.20%, 0.21% and 0.0072%, respectively. At Site 5, the sedimentary organic carbon, nitrogen and phosphorus concentrations in the top 10 cm of sediment were 2.44%, 0.29% and 0.0125%, respectively. Tabulated values for sedimentary organic matter at all the sampling sites are presented in Appendix A. In all cases, except for the predicted N_o value at Site 5, the values predicted for the metabolizable organic carbon, nitrogen and phosphorus at the sediment/water interface exceed the total sedimentary values for this material. This is, of course, impossible if measured sedimentary organic matter is the sole source of energy for sulphate reducing bacteria. Two possibilities exist: 1) the kinetic model is not applicable for Great Bay sediments or 2) the measured sedimentary organic matter is not a good indicator of the total material available for metabolism by sulphate reducing bacteria.

Using the calculated rate constants and values for G_o, N_o and P_o, as well as coefficients from the fitted equations for sulphate, ammonia and phosphate and constants presented earlier, the actual rates of sulphate reduction and ammonia and phosphate production may be cal-

culated using the following equations:

1) Rate (SO_4^{2-}) = L F k_S C_o exp $((-k_S/\omega)X)$;

2) Rate (NH_4^{+}) = F k_N N_o exp $((-k_N/\omega)X)$;

3) Rate (PO_4^{3-}) = F k_p P_o exp $((-k_p/\omega)X)$;

Berner (1980). These calculations were made using the data from the two Footman Island (Site 4), and one Squamscott River (Site 5), cores, and the results for various depths in these cores are presented in Table 4-6. The depths chosen for these calculations represent the mid-points for each core section.

Reaction rates for sulphate reduction, and ammonia and phosphate production were found to decrease with depth, as forced by the model. At the Footman Islands location (Site 4), sulphate reduction rates were considerably higher in the top 30 cm of sediment in August compared to October. This is undoubtably due to the bacterial response to cooler water temperatures in the fall. Below 30 cm, sulphate reduction rates were actually higher in the fall core. This may be due to warmer temperatures in these deeper sediments in the fall. Alternatively, the buildup of bacterial inhibitors (e.g. H_2S), in deep sections of sediment cores during the summer may result in the lower sulphate reduction rates in the summer relative to fall. The reaction rates for sulphate in the surface sediments at Site 5 in July were somewhat lower than those observed in the August core from Site 4; 9.7 nmoles/l-yr. versus 31 nmoles/l-yr. As mentioned earlier, this may be a consequence of the greater lability of the organic matter deposited at Site 4 compared to Site 5. Below a depth of 30 cm in the sediment, sulphate reduction rates were found to be greater at Site 5 than at Site 4. Again, this is probably due to the diffusion of sulphate to greater depths at Site 5, given the

Table 4-6. Reaction rates of sulphate reduction and ammonia and phosphate production for two cores from Site 4 (Footman Islands), and a core from Site 5 (Squamscott River).

Site 4 (August)

Depth (cm)	Reaction Rates (mmoles/l-yr.) R_S	R_N	R_P
7.5	31	1.6	0.011
22.5	7.8	1.0	0.0097
37.5	0.86	0.69	0.0089
52.5	0.14	0.45	0.0082
67.5	0.023	0.30	0.0075

Site 4 (October)

Depth (cm)	Reaction Rates (mmoles/l-yr.) R_S	R_N	R_P
7.5	4.3	0.017	0.057
22.5	2.5	0.017	0.021
37.5	1.5	0.017	0.0075
52.5	0.8	0.017	0.0027
67.5	0.52	0.017	0.00098

Site 5 (July)

Depth (cm)	Reaction Rates (mmoles/l-yr.) R_S	R_N	R_P
7.5	9.7	0.13	0.0076
22.5	6.5	0.12	0.0076
37.5	4.3	0.11	0.0076
52.5	2.9	0.10	0.0076
67.5	1.9	0.091	0.0075

slower sulphate reduction rates in the surface sediments here.

The rates of ammonia production were found to be greater at all depths at Site 4 in August than in October. This again illustrates the effect of decreased sediment and overlying seawater temperatures on bacterial activities. As with sulphate reduction rates, the rates of ammonia production were found to be greater at Site 4 than Site 5. Phosphate production rates were also observed to be greater at Site 4. However, unlike the other reaction rates, the rates of phosphate production in the top 30 cm of sediment at Site 4 were actually somewhat higher in October than in August.

The sulphate reduction rates calculated in this study were, on average, about five times as high as those calculated by Goldhaber et al. (1977), for a site in Long Island Sound (e.g. the FOAM Site), using a similar modelling approach. Similarly, the rates of ammonia production for Great Bay presented in Table 4-6 were considerably higher than those estimated by Rosenfeld (1981), for the FOAM Site. No calculated rates of phosphate production have been published for comparison to the values obtained here. The probable cause of the higher rates of sulphate reduction and ammonia production in Great Bay compared tc those calculated for the FOAM Site is the closer proximity of the Great Bay Estuary to land. Indeed, Rosenfeld (1981), calculated ammonia production rates for a site closer to land in Long Island Sound (e.g. the Sachem Site), and found these rates to be considerably higher than those observed at the FOAM Site. Proximity to land often results in greater amounts of organic matter deposited in the sediments. In addition to this 'land effect', the type of organic matter deposited in the sediments may also greatly affect the rates of bacterial activity (Berner,

1964, 1970 and 1978; Goldhaber and Kaplan, 1975; Martens and Goldhaber, 1978; and Lyons and Gaudette, 1979). Thus, the very high sulphate reduction and ammonia production rates in the surface sediments of Site 4 in Great Bay probably reflects the input of a readily degradable source of organic matter to the sediments from the eelgrass bed at this site (Lyons and Gaudette, 1979).

Hines (1981), has measured the actual rates of sulphate reduction at Sites 3 and 5 in Great Bay (i.e. Adams Cove and Squamscott River locations), using the ^{35}S technique. His results indicated rates of about 50 mmoles/l-yr at Site 3 and 11 mmoles/l-yr at Site 5 in the top 12 cm of sediment during the summer months. These results are very similar to those predicted using the kinetic model for the 7.5 cm depth sediment section at Sites 4 and 5 during the summer months (see Table 4-6). In addition, 'jar' experiments (see Goldhaber et al., 1977 for a discussion of 'jar' experiments), using surface sediments from Sites 3 and 5 in Great Bay provided sulphate reduction rate estimates for these sediments of about 57 mmoles/l-yr and 4.7 mmoles/l-yr , respectively (Hines et al., 1980). Again, these results are strikingly similar to those provided by the kinetic model. This is strong evidence that the kinetic model is applicable to Great Bay sediments, and provides valid estimates of the bacterial reaction rates.

However, if the calculated sulphate reduction and ammonia and phosphate production rates are correct, the problem of explaining the anamolously high G_O, N_O and P_O values remains. The calculated values for the metabolizable organic carbon, nitrogen and phosphorus in the surface sediments (i.e. G_O, N_O and P_O), exceeded the measured total sedimentary organic carbon, nitrogen and phosphorus to a considerable

degree. Dissolved organic matter may be utilized by sulphate reducing bacteria in addition to the sedimentary organics, however, DOC only accounts for about 0.02% by weight of wet sediment and cannot account for the discrepancy between the predicted and measured values. Murray and co-workers (1978), also obtained anamolously high G_o values from similar calculations using sulphate data from Saanich Inlet, British Columbia pore waters. These workers explained this discrepancy in terms of the diffusion of additional organic carbon from below in the form of methane. As mentioned in Chapter 1, methane may be utilized by sulphate reducing bacteria as a carbon source (Martens and Berner, 1977). The significance of this source of organic carbon for sulphate reducing bacteria in Great Bay sediments is uncertain, although recent work has shown that methane production is occurring here (Hines, personal communication). In any event, this source would not account for the anamolously high N_o and P_o values. Thus, some source of organic C, N and P other than sedimentary organic matter and methane must also be utilized by sulphate reduction. However, the nature of this source is uncertain and must await future work.

III. Conclusions

In this chapter, a general overview of many of the diagenetic processes occurring in Great Bay anoxic sediments and pore waters has been presented. Based on sediment size and sedimentary organic matter depth profiles, sedimentation in Great Bay appears to have been non-steady state in the past. Despite this, pore water profiles of many species indicative of bacterial sulphate reduction and the degradation of organic matter (e.g. titration alkalinity, ammonia, phosphate and

sulphate), in Great Bay are similar to those observed by other workers in areas of steady state sedimentation (Goldhaber and Kaplan, 1975; Goldhaber et al., 1977; Martens et al., 1978; and Rosenfeld, 1978). This supports the idea that the rates of sulphate reduction in marine sediments are better correlated with the type of organic matter present, rather than the total amount (Berner, 1964 and 1970; Goldhaber and Kaplan, 1975; and Lyons and Gaudette, 1979).

An extensive array of data on the vertical, lateral and seasonal variations of titration alkalinity, pH, chloride, sulphate, ammonia, phosphate and total dissolved iron were presented. Very high concentrations of titration alkalinity, ammonia and phosphate were observed in Great Bay pore waters, especially at Sites 4 (Footman Islands), and 5 (Squamscott River). Fresh groundwater was observed in the pore water at Site 3 (Adams Cove), and seemed to have a diluting effect on most chemical species produced as a consequence of the bacterial degradation of organic matter. Large seasonal changes in the pore water concentrations of titration alkalinity, ammonia and phosphate at depths of 15 to 90 cm in the sediments were observed. The decreased concentrations of these chemical species in the fall and winter cannot be accounted for by molecular diffusion, since this process is too slow (Krom and Berner, 1980). A temperature regulated adsorption/desorption process was hypothesized to account for the observed seasonal trends.

Seasonal variations in titration alkalinity, ammonia, phosphate, total dissolved iron and dissolved organic carbon were also observed in the top 15 cm at Site 3. These variations were interrelated through redox-mediated dissolution and precipitation reactions and bioturbation. A summary of these seasonal changes, produced by averaging all values

in the top 12 to 15 cm of each core, is presented in Figure 4-31. In the early spring, heterotrophic bacterial activity increased, resulting in the consumption of dissolved organic carbon, a lowering of Eh and a concomitant dissolution of iron. By May, increasing sulphate reduction produced higher pore water values of dissolved organic carbon, ammonia and phosphate, and precipitation of iron from the pore water by the probable formation of iron sulphides. The decreased concentrations of all of these chemical species during the summer months was a direct consequence of increased bioturbation.

The molecular size distribution of total dissolved iron in Great Bay pore waters was investigated using ultrafiltration and coarse filtration techniques. The results of this study indicated that the dissolved iron in these pore waters was primarily colloidal in nature (e.g. >50,000), either complexed to large organic polymers (Lyons et al., 1979a), or present as an inorganic colloid.

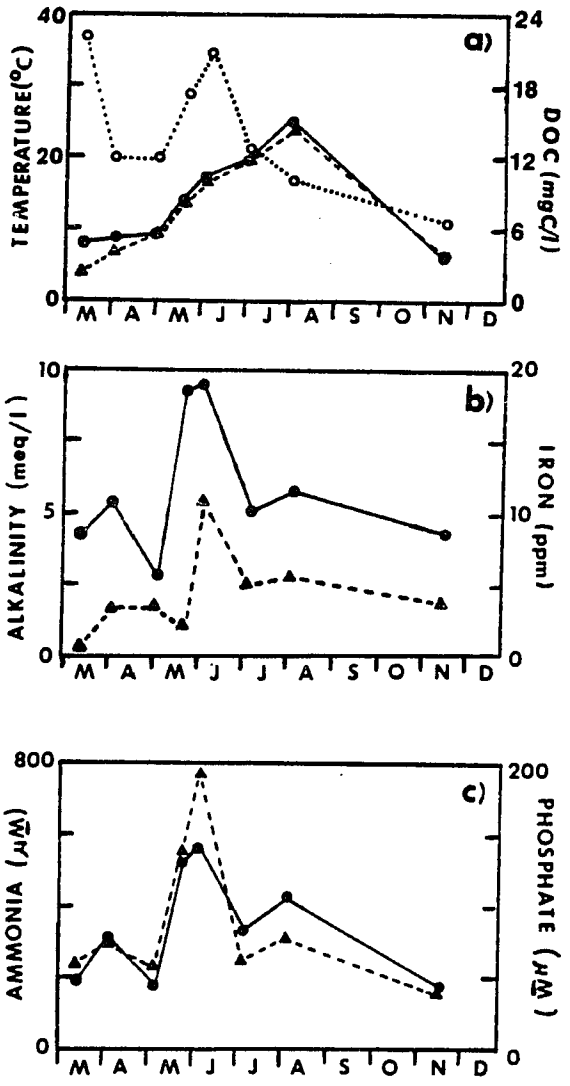

Figure 4-31. The seasonal variation (March to December, 1980), of a number of chemical species in pore waters, and sediment and overlying water temperatures at Site 3 (Adams Cove): a) sediment (●—●), and overlying water (▲---▲), temperatures (C^{o}), and pore water DOC concentrations (o---o), (mgC/l); b) iron (●—●), (ppm), and titration alkalinity (▲---▲), (meq/l), pore water concentrations; and c) ammonia (●—●), (μM), and phosphate (▲---▲), (μM), pore water concentrations. Each point represents an average value for the top 12 cm of sediment.

CHAPTER 5

DISSOLVED ORGANIC CARBON IN ANOXIC ESTUARINE PORE WATER

I. Introduction to Problem

In the past, studies of the organic chemistry of seawater and other natural water environments have used two different approaches: 1) the quantitative analysis of specific organic compounds and 2) a more qualitative approach, loosely termed gross organic analysis. In seawater more work has been done using the former approach; and a number of compounds or classes of compounds have been determined, including amino acids (Gardner, 1978), carbohydrates (Johnson and Sieburth, 1977), sterols (Gagosian, 1975), fatty acids (Treguer et al., 1972), and chlorinated hydrocarbons (Risebrough, 1971), to name a few. In the pore water of marine sediments less has been accomplished, although a number of organic compounds have been measured in this evnironment as well (e.g. amino acids (Henrichs and Farrington, 1979), carbohydrates (Lyons et al., 1979c), and fatty acids (Miller et al., 1979). Lee and Bada (1977), have emphasized the importance of studies focusing on specific and especially biologically active organic compounds in the sea for understanding the process of bacterial utilization of organic matter. These bacterial processes, both in the water column and in the sediments are largely responsible for regenerating inorganic nutrients and for determining the ultimate fate of organic species (Berner, 1971; and Morris and Eglinton, 1977).

However, as Sharp (1975), has pointed out, studies of specific organic compounds in seawater and pore water have, as yet, accounted for less than 10% of the total organic matter present. Nor is this percentage likely to increase dramatically in the near future, given the enormous number of organic species potentially present (Faulkner and Anderson, 1974; and Yen, 1975). Clearly, studies of the total or gross organic matter present in seawater and pore water are needed, in addition to work on specific organic compounds. Research emphasizing gross organic analysis will be needed to establish better estimates of the global balances of the elements carbon, nitrogen and phosphorus. In addition, qualitative studies of the nature of the organic matter present in natural waters are necessary for comprehending such processes as petroleum genesis and organic matter/trace metal interactions.

The emphasis in this chapter is on the distribution of dissolved organic carbon (DOC), in the pore water of estuarine sediments from Great Bay, New Hampshire. Although a number of previous workers have reported concentrations of DOC from the pore water of nearshore marine sediments (see Table 5-1), no systematic study of the distribution of DOC in pore water has been reported. The major goals of this study were to investigate the lateral, vertical and seasonal variations of DOC and its molecular size distribution in order to glean a greater understanding of the dynamics and nature of organic matter in anoxic marine sediments. Sampling sites and procedures, processing methods, analysis of DOC and ultrafiltration techniques have been described earlier (see Chapter 2).

Table 5-1. Ranges of dissolved organic carbon (DOC), values from pore waters of nearshore marine sediments (adapted from Lyons et al. (1979)).

Range of DOC Values (mgC/l)	Location	Reference
42 - 148	Saanich Inlet, B.C.	Nissenbaum et al. (1972)
25 - 390	Toledo, Or.	Bella (1972)
6 - 10	Mobile Bay, Ala.	Lindberg and Harriss (1974)
24 - 77	Everglades, Fla.[1]	Lindberg and Harriss (1974)
4 - 42	Airplane Lake, La.	Whelan et al. (1976)
8 - 66	Loch Duich, Scotland	Krom and Sholkovitz (1977)
40 - 150	White Oak Estuary, N.C.	Martens and Goldhaber (1978)
12 44	Branford Harbor, Ct.	Lyons et al. (1978)
8 - 115	Noank, Ct.	Lyons et al. (1978)
2 - 130	Great Bay, N.H.	Lyons et al. (1978)
4 - 19	Bermuda Islands[1]	Lyons et al. (1979c)
5 - 224	Great Bay, N.H.	This Work

1) Carbonate rich sediments.

II. Results and Discussion

A. Vertical and Lateral Variations of DOC

Concentrations of DOC for a number of cores from all five sampling sites in Great Bay (see Figure 2-2), are presented in Table 5-2. These data are plotted as functions of depth in Figure 5-1. For purposes of comparison, all cores presented here were obtained during the summer months. Concentrations of DOC were observed to range from less than 10 mgC/l to greater than 200 mgC/l in these cores. These values compare favorably with ranges of DOC observed by other workers in the pore water of marine sediments (Table 5-1). In contrast, overlying seawater DOC concentrations were determined to be in the range of 1-3 mgC/l. This indicates the presence of some mechanism in these sediments for the autochthonous production of DOC from sedimentary organic matter. Since the accumulation of DOC in the pore water is accompanied by analogous increases in alkalinity, ammonia and phosphate (see Chapter 4), the production of DOC in the pore water is undoubtably bacterially mediated (Berner, 1971; Krom and Sholkovitz, 1977; and Lyons et al., 1980). It has been suggested that this production of DOC from sedimentary organic matter is entirely the result of fermentation (Toerien and Hattingh, 1969; Otsuki and Hanya, 1972; Doelle, 1975; and Martens and Goldhaber, 1978). However, a linear relationship between DOC and dissolved sulphate was observed in a series of three cores from Site 4 at sulphate concentrations greater than about 2.5 mM. This correlation is illustrated in Figure 5-2. Thus, sulphate reducing bacteria appear to play a role in controlling the DOC concentrations of Great Bay pore waters, probably by acting as the primary consumers of this material. By including values for DOC and dissolved sulphate at sulphate concentra-

Table 5-2. Dissolved organic carbon concentrations from five sampling sites in Great Bay, New Hampshire.

Site 1 (Piscataqua River)

Core PS-III
Date: 7-19-78

Depth (cm)	DOC (mgC/l)
0-5	63.9
5-10	48.0
10-20	64.6
20-30	62.3
30-35	89.6

Core UF-VI
Date: 8-11-80

Depth (cm)	DOC (mgC/l)
0-10	34.5
10-20	44.8
20-30	77.2

Site 2 (Welsh Cove)

Core PS-I
Date: 6-10-78

Depth (cm)	DOC (mgC/l)
0-5	40.5
5-10	20.8
10-15	21.3
15-20	23.3
20-25	23.9
25-30	26.9
30-35	30.4
35-40	32.1
40-45	40.1
45-50	36.8
50-55	36.8

Site 3 (Adams Cove)

Core KW-I
Date: 6-20-79

Depth (cm)	DOC (mgC/l)
0-10	31.1
10-20	8.5
20-30	23.0
30-40	36.3
40-50	49.2
50-60	206.7

Core UF-IV
Date: 7-11-80

Depth (cm)	DOC (mgC/l)
0-15	8.3
15-30	10.2
30-45	18.7
45-60	14.8
60-75	200.2
75-90	19.8

Table 5-2. continued.

Site 4 (Footman Islands)

Core PS-II Date: 6-30-78		Core OAX-I Date: 6-23-80	
Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)
0-5	49.1	0-15	14.3
5-10	49.2	15-30	29.1
10-20	67.9	30-45	46.5
20-30	65.0	45-60	46.7
30-40	66.8	60-75	46.1
40-50	101.0	75-90	50.1
50-60	97.9		
60-70	107.0		
70-80	118.0		
80-85	109.0		

Site 5 (Squamscott River)

Core PS-IV Date: 8-10-78		Core UF-V Date: 7-11-80	
Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)
0-10	52.4	0-15	7.6
10-20	84.5	15-30	24.6
20-30	107.0	30-45	47.3
30-40	144.0	45-60	58.3
40-50	144.1	60-75	71.4
50-60	137.3		
60-70	156.9		
70-80	136.8		
80-90	-		
90-100	75.4		

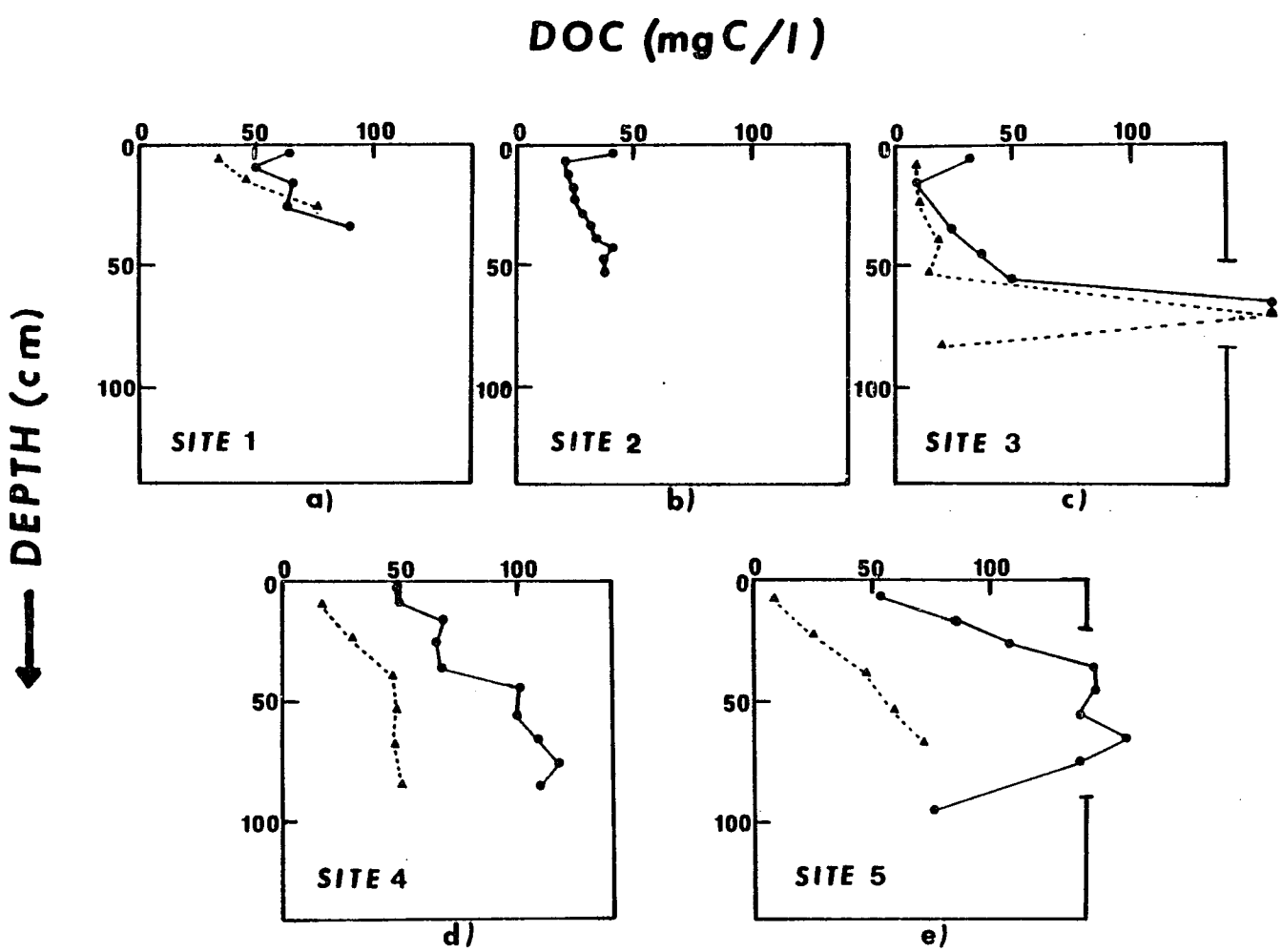

Figure 5-1. DOC concentrations (mgC/l), versus depth (cm), for five sites in Great Bay, New Hampshire: a) Site 1 (Piscataqua River), 7-19-78 (●—●), and 8-11-80 (▲---▲); b) Site 2 (Welsh Cove), 6-10-78 (●—●); c) Site 3 (Adams Cove), 6-20-79 (●—●), and 7-11-80 (▲---▲); Site 4 (Footman Islands), 6-30-78 (●—●), and 6-23-80 (▲---▲); Site 5 (Squamscott River), 8-10-78 (●—●), and 7-11-80 (▲--▲).

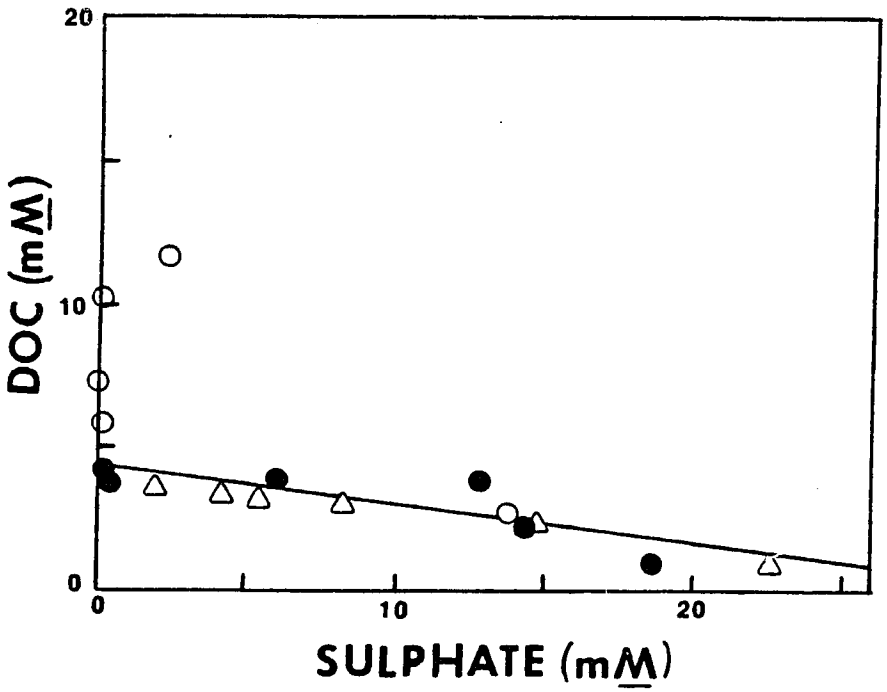

Figure 5-2. Plot of SO_4^{2-} (mM), versus DOC (mM), for three cores from Site 4 (Footman Islands): Core OAX-I (●), 6-23-80; Core UF-VII (o), 8-11-80; and Core OAX-II (△), 10-21-80. A linear correlation was observed at sulphate concentrations above 2.5 mM : $y = -0.134x + 4.37$ ($r^2 = 0.688$).

tions of less than 2.5 mM in this calculation, a much poorer correlation was obtained ($r^2 = 0.409$). It has been suggested that below dissolved sulphate concentrations of about 2 mM, sulphate reduction becomes sulphate limited (Berner, 1970), and below this concentration other bacterial metabolic processes (e.g. methanogenesis), probably control observed DOC values.

The most obvious relationship observable in Figure 5-1 is the general increase in DOC with increasing depth in these cores. Although some variations from this trend were observed, these are generally due to environmental factors (e.g. sand layers or freshwater intrusion), unrelated to diagenesis. This same relationship has been observed by previous workers in nearshore clastic sediments (Krom and Sholkovitz, 1977; Lyons et al., 1978; and Martens and Goldhaber, 1978). Offshore clastic sediments have also shown increasing DOC concentrations with depth (Lyons et al., 1980); but at considerably lower absolute levels compared to nearshore values (due to lower sedimentation rates offshore). However, this same trend has not been observed in carbonate sediments (Lyons et al., 1979c).

It is, perhaps, surprising that DOC concentrations are observed to increase with depth, considering that the maximum rates of bacterial activity occur in the top 5 cm of sediment (Sorokin, 1962; and Hines, 1981). Based on this, it might be expected that maximum production of DOC from sedimentary organic matter would occur at the surface. In fact, there is evidence in some of the profiles in Figure 5-1 (e.g. the core from Site 2), of significant production of DOC in the surficial sediments. However, in the surface sediments there are also a number of processes which tend to remove large amounts of DOC from the pore water

to the overlying seawater, including bioturbation, advection from wave and tidal action and diffusion (Rhoads, 1967; Li and Gregory, 1974; Berner, 1976; Goldhaber et al., 1977; Rhoads et al., 1977; Vanderborght et al., 1977a; Grundmanis and Murray, 1977; Aller and Yingst, 1978; Aller, 1978; and Hines, 1981). Deeper in the sediments, production of DOC may occur at much slower rates than at the surface, but accumulation of this material in the pore water is possible due to the absence of removal processes with the exception of diffusion, which is very slow (Wollast and Garrels, 1971; and Vanderborght et al., 1977a and 1977b). Indeed, it may even be argued that diffusion of DOC in anoxic marine sediments is a negligible process, given the large average molecular size (see below), and the likely high surface activity of the DOC present in the pore water (Eglinton and Murphy, 1969; and Nissenbaum et al., 1972), which would prevent this material from diffusing in the manner of an ionic species.

A second factor which may contribute to the greater DOC concentrations at depth is the decreasing porosity with depth generally observed in marine sediments (Vanderborght et al., 1977a; and Johnson and Key, 1981). Thus, DOC produced from sedimentary organic matter at depth by bacterial activity dissolves in a smaller volume of fluid than in surficial sediments, resulting in higher DOC concentrations at depth.

One interesting feature of the depth profiles from Site 3 (Figure 5-1), is the extremely high DOC concentration observed between 60 and 70 cm in both cores. Sedimentary organic carbon analyses revealed no indication of any anomaly (e.g. the presence of a peat layer), in the organic matter content of the sediment at this depth (see Chapter 4). However, chloride analyses of one of these cores indicated the

presence of freshwater intrusion from below at this site (see Chapter 4). Two explanations may account for these anomalously high DOC concentrations: 1) increased solubility of sedimentary organic matter in fresh versus seawater, as suggested by Lammela (1981); and 2) oxidation of sedimentary organic matter by oxic groundwater, resulting in increased solubility of this material as discussed in Chapter 3. It is unknown which of these factors may predominate, and it may be that the effects of both are being observed.

The lateral variation of DOC in anoxic pore water from Great Bay was observed to be linerally related to the amounts of organic matter in the sediments. Correlations of DOC and sedimentary organic carbon, nitrogen and phosphorus percentages for all five sites are illustrated in Figure 5-3. These points were observed to congregate into two groups; with Sites 1, 2 and 3 containing lower amounts of sedimentary organic matter and, consequently, lower DOC concentrations in the pore water relative to Sites 4 and 5. The reasons for the lower percentages of sedimentary organic matter at Sites 1, 2 and 3 were discussed in Chapter 4. Previous workers have suggested that the rates of bacterial sulphate reduction in anoxic marine sediments are directly proportional to the amounts of metabolizable organic matter in the sediments (Berner, 1964 and 1970). However, more recent results have indicated that the nature (e.g. biological reactivity), of the organic matter in the sediments may be a more sensitive indicator of the rates of sulphate reduction than is the total amount of sedimentary organic matter present (Goldhaber and Kaplan, 1975; Lyons and Gaudette, 1979; and Berner, 1978). This would suggest that the nature of the organic matter at all five sampling sites in Great Bay is similar, assuming

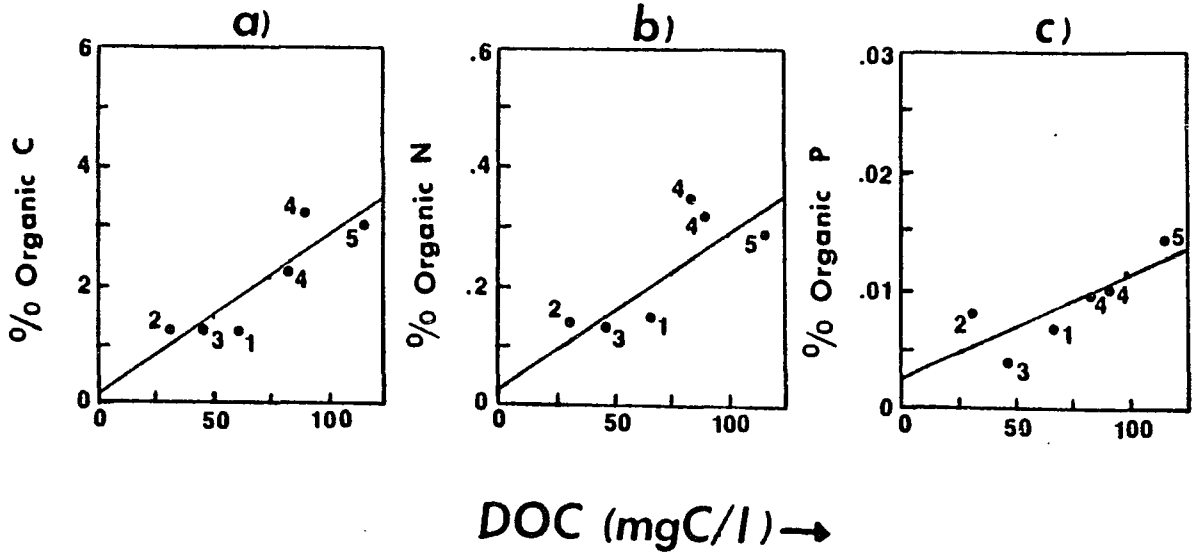

Figure 5-3. Correlations of DOC (mgC/l), versus sedimentary organic matter (%): a) DOC versus sedimentary organic carbon ($y = 2.60 \times 10^{-2}(x) + 0.159$; $r^2 = 0.747$); b) DOC versus sedimentary organic nitrogen ($y = 2.52 \times 10^{-3}(x) + 0.0326$; $r^2 = 0.501$; and c) DOC versus sedimentary organic phosphorus ($y = 8.81 \times 10^{-5}(x) + 0.00250$; $r^2 = 0.664$). The numerals adjacent to each data point indicate the sampling sites.

that these results concerning sulphate reduction rates also apply to the rates of bacterial fermentation, which produces the DOC. Berner (1978), has suggested that if organic remains of essentially the same biochemical character serve as the source material for sedimentary organic matter in a given area, a constant ratio of reactive to total organic matter in all the sediments of this area should exist. This implies a common source material for all five Great Bay sites in this study. Carbon isotope work (e.g. using C^{13}), has indicated that most estuarine sediments contain organic matter from terrestrial and marine sources (Hedges and Parker, 1976; Pocklington, 1976; Shultz and Clader, 1976; and Fry et al., 1977). This result is supported by δC^{13} values (Parker et al., 1972), of sediment from two Great Bay sites (Sites 3 and 5 in this study), which suggest both a marine and terrestrial source for the organic matter in these sediments (Templeton, 1980).

B. Seasonal Variation of DOC

Concentrations of DOC in the top 12 cm of sediment from 12 box cores taken at Site 3 (Adams Cove), from July 1979 to November 1980 at irregular intervals are presented in Table 5-3. These data are illustrated in Figure 5-4. Over this period, DOC concentrations ranged from 4.7 to 41.5 mgC/l. From July to September 1979, values of DOC were observed to decrease slightly, possibly a result of decreased bacterial activity coupled with increased bioturbation. Despite lower bacterial activity observed during the winter months (Hines, 1981), DOC concentrations were observed to increase from September 1979 to February 1980. Apparently, although formation of DOC from sedimentary organic matter is slowed during the colder months of the year, accumulation of DOC in the pore water occurs due to the lack of bioturbation

Table 5-3. Seasonal variation of DOC in the top 12 cm of sediment at Site 3 (Adams Cove).

Date	7-10-79	9-6-79	12-10-79	2-18-80
Depth (cm)	DOC (mgC/l)	DOC (mgC/l)	DOC (mgC/l)	DOC (mgC/l)
0-2	20.3	14.7	11.8	19.1
2-4	16.9	12.2	14.3	22.8
4-6	17.0	13.3	14.6	35.1
6-8	18.2	15.9	18.7	34.7
8-10	17.9	15.7	20.0	33.7
10-12	20.3	18.3	25.1	28.7

Date	3-10-80	4-9-80	5-20-80	5-20-80
Depth (cm)	DOC (mgC/l)	DOC (mgC/l)	DOC (mgC/l)	DOC (mgC/l)
0-2	41.5	10.2	12.0	13.2
2-4	14.7	8.1	9.6	18.8
4-6	12.0	11.5	8.6	16.2
6-8	21.8	13.0	9.8	18.9
8-10	22.3	14.9	10.5	19.8
10-12	19.4	14.4	20.9	17.8

Date	6-2-80	7-2-80	8-1-80	11-14-80
Depth (cm)	DOC (mgC/l)	DOC (mgC/l)	DOC (mgC/l)	DOC (mgC/l)
0-2	11.3	8.7	6.4	4.7
2-4	14.0	-	7.4	5.0
4-6	17.4	10.3	8.2	5.2
6-8	22.7	13.3	10.4	6.1
8-10	27.5	14.2	11.7	6.9
10-12	31.7	14.3	13.7	10.0

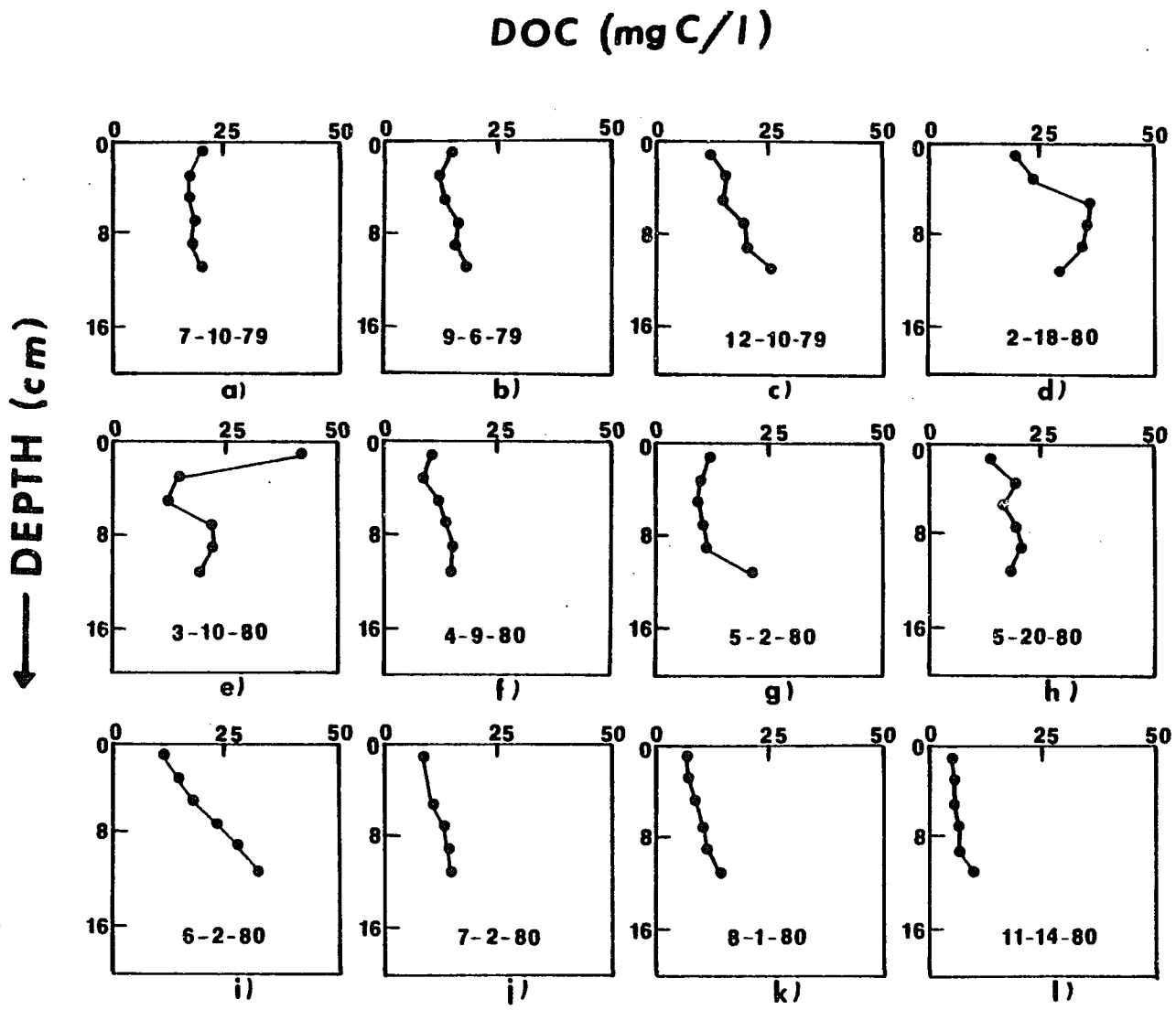

Figure 5-4. Seasonal variation of DOC in the top 12 cm of sediment at Site 3 (Adams Cove).

during the winter. In addition, ice cover during the winter may damp out much of the wave and tidal action which act as advective removal mechanisms for DOC in the pore water during warmer months.

During the period from February to May 2, 1980, whole core averages of DOC were observed to steadily decrease. However, in the top 2 cm of sediment a peak DOC concentration of 41.5 mgC/l was observed in the March 1980 core. This peak value may have resulted from bacterial degradation of the organic remains of an early season phytoplankton bloom (Fogg, 1975; and Hines, personal communication). The steady decline in whole core DOC concentrations from February to mid May could have been due to advective removal of DOC from the pore water as a result of increased wind and more storms in the early spring. However, concentrations of NH_4^+ and PO_4^{3-} in the pore water were observed to increase over this same period in these cores (see Chapter 4). This observed decrease in whole core average DOC values was more likely a result of increasing heterotrophic bacterial activities over this period (Hines, 1981). From May 2, 1980 to June 2, 1980, steady increases in pore water DOC concentrations were observed undoubtably as a result of increased fermentation as the sediment temperatures warm (see Chapter 4). However, with the advent of increased bioturbation in mid June (Lyons, personal communication), DOC concentrations in the pore water showed a sharp decline from June 2 to July 2, 1980; and continued to decrease through November, 1980 (the final core in this series). This paralleled the trend observed the preceeding fall.

A somewhat different seasonal trend in DOC concentrations in the top 12 cm of sediment was observed at Site 4 (Footman Islands), during 1979. These data are tabulated in Table 5-4 and illustrated

Table 5-4. Seasonal variation of DOC in the top 12 cm of sediment at Site 4 (Footman Islands).

Date	4-26-79	6-10-79	7-23-79	9-12-79
	DOC	DOC	DOC	DOC
Depth (cm)	(mgC/l)	(mgC/l)	(mgC/l)	(mgC/l)
0-2	25.7	24.2	224.1	77.7
2-4	15.6	17.1	143.0	90.6
4-6	16.6	38.1	117.5	140.9
6-8	17.3	41.3	126.4	127.8
8-10	23.7	17.9	138.1	126.0
10-12	23.9	25.7	53.5	129.1

in Figure 5-5. As at Site 3 (Adams Cove), modest increases in concentrations of DOC in the pore water were observed during the spring (April 26 to June 10, 1979), at the Footman Islands location. However, whereas bioturbation resulted in lower DOC pore water values after mid June at Site 3, no such effect was observed at the Footman Islands site until September 1979. Accumulation of DOC in the pore water resulted in extremely high values (up to 224 mgC/l), in the July 1979 core at Site 4. It is unclear whether these high concentrations resulted from very high bacterial activity at the Footman Islands site, or from a lack of bioturbation here. It is interesting to note the trend of decreasing DOC concentrations with depth in this core. This is directly opposite to the trend that is normally observed for DOC in anoxic marine sediments (discussed above); and emphasizes the contention that maximum bacterial activity occurs in the surficial sediments.

Concentrations of DOC in deep sediment cores collected over a two year period at Site 4 (Footman Islands), are presented in Table 5-5 and Figure 5-6. The seasonal trend observed in these cores follows that expected based on the idea of higher bacterial activity (and higher DOC production), during the warmer months of the year. For example, whole core average DOC concentrations increased from 56.9 mgC/l in April to 112.0 mgC/l in late June 1979; and then decreased to 33.1 mgC/l in late October 1979. A similar trend was observed for spring, summer and fall cores during 1980. The rather erratic vertical distribution in the core obtained on June 20, 1979 (Figure 5-6b), is difficult to explain, considering the relatively smooth vertical profiles observed in most other cores. This core was processed in exactly the same fashion as all the others, however, it is possible that some

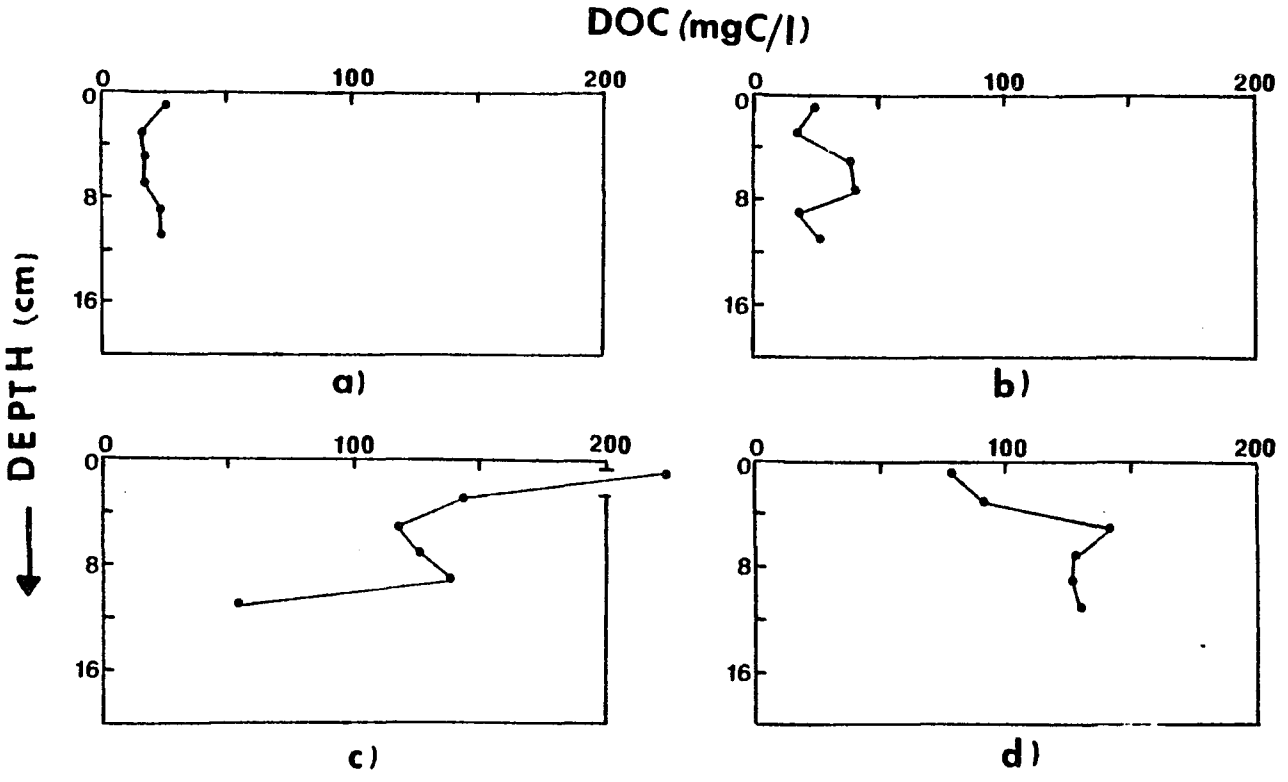

Figure 5-5. Seasonal variation of DOC (mgC/l) in the top 12 cm of sediment at Site 4 (Footman Islands): a) 4-26-79; b) 6-10-79; c) 7-23-79; and d) 9-12-79.

Table 5-5. Seasonal variation of DOC in deep cores at Site 4 (Footman Islands).

Date	4-6-79		6-20-79		10-30-79	
	Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)
	0-10	59.7	0-10	166.3	0-10	17.7
	10-20	70.1	10-20	52.6	10-20	16.6
	20-30	66.5	20-30	53.9	20-30	35.4
	30-40	63.8	30-40	98.6	30-40	31.2
	40-50	44.4	40-50	78.9	40-50	35.9
	50-60	51.4	50-60	127.6	50-63	36.4
	60-70	56.4	60-70	74.4	63-73	42.4
	70-80	54.3	70-80	118.1	73-83	43.4
	80-90	45.6	80-90	63.6	83-93	38.9
			90-100	83.8		

Date	6-23-80		8-11-80		10-21-80	
	Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)
	0-15	14.3	0-15	34.9	0-15	14.1
	15-30	29.1	15-30	141.4	15-30	29.4
	30-45	46.5	30-45	70.1	30-45	38.7
	45-60	46.7	45-60	76.6	45-60	38.9
	60-75	46.1	60-75	123.1	60-75	39.4
	75-90	50.1			75-90	41.9

Date	4-15-81		5-28-81	
	Depth (cm)	DOC (mgC/l)	Depth (cm)	DOC (mgC/l)
	0-15	18.9	0-15	10.6
	15-30	46.8	15-30	21.0
	30-45	52.2	30-45	30.7
	45-60	50.9	45-60	31.3
	60-75	46.2	60-75	32.9
			75-90	31.9

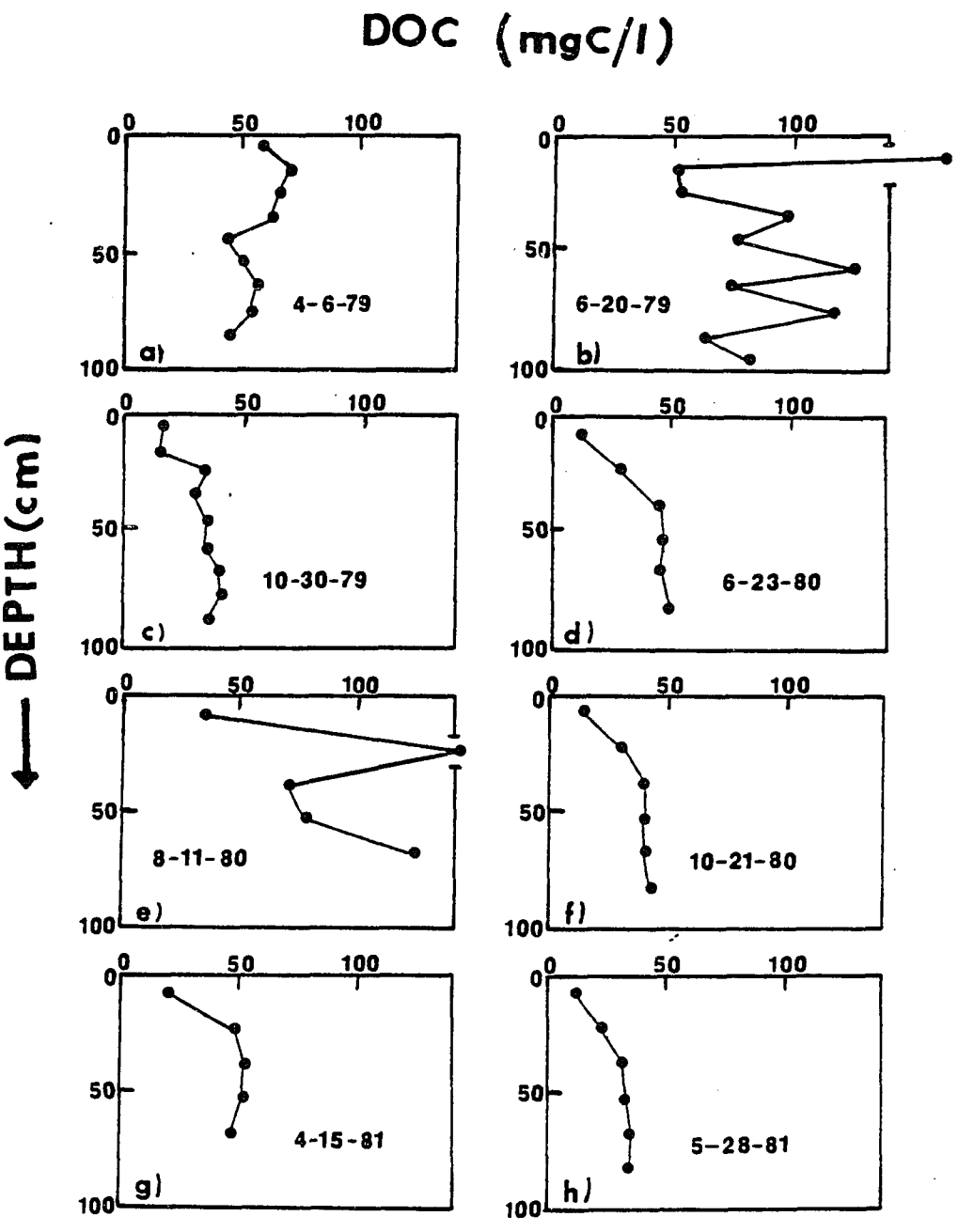

Figure 5-6. Seasonal variation of DOC in deep cores from Site 4 (Footman Islands).

changes may have taken place during processing or storage to cause the unusual profile. It is also possible that this core simply had an unusual vertical distribution of DOC.

The seasonal effects observed in the upper sediment sections of these cores were not unexpected considering temperature effects on bacterial activity, and the mechanisms for removal of DOC from the pore water at the surface. However, the large seasonal changes in DOC concentrations in the pore water from deeper core sections (e.g. especially below 30 cm), were surprising. These changes are probably not a result of lateral variability (see Chapter 2), but appear to be due to a seasonal effect. Bacterial numbers and activities decrease rapidly in anoxic marine sediments below the sediment/water interface, becoming negligible below a depth of 10 cm (Sorokin, 1962; Hines and Buck, 1981; and Hines, 1981). This makes it difficult to explain the observed seasonal changes in DOC by a bacterial mechanism. Even if one accepts the concept of considerable bacterial activity at depth during the summer months, there is still the question of where the DOC goes in the fall. As discussed earlier, neither advective nor diffusive mechanisms are likely to remove significant quantities of DOC below the upper 20 or 30 cm of sediment. It seems likely, then, that some physical process is responsible for the seasonal changes of DOC in the pore water deep in anoxic sediments. One possible explanation is a temperature induced solubility effect on DOC. Higher pore water temperatures during the summer may induce increased dissolution of sedimentary organic matter. Conversely, decreased temperatures during cooler months may result in removal of DOC from the pore water. Reeburgh (1968), observed deep sediments to be relatively well buffered from seasonal temperature

effects. However, recent work (Hines, 1981; and Westrich and Berner, 1981), has shown that significant seasonal temperature changes may be observed below 30 cm in nearshore marine sediments. For example, Westrich and Berner (1981), observed temperature ranges of 7°C to 20°C and 2°C to 18°C for sediments at a depth of 60 cm at two sites in Long Island Sound (i.e. the FOAM and NWC sites, respectively). Hines (1981), has observed similar temperature ranges for deep sediments from Site 3 in Great Bay.

The observation that a large proportion of the DOC in anoxic estuarine pore waters is colloidal in nature (see discussion below), lends credance to this proposed temperature induced solubility effect. The solubility of such high molecular weight material would be expected to be more sensitive to temperature changes, than organic compounds of lower molecular weight (Moore, 1972). Furthermore, Templeton (1980), and Lammela (1981), were able to extract significant quantities of organic matter from Great Bay anoxic sediments using an artificial seawater extractant and a simple shaking technique. This suggests that a large proportion of the sedimentary organic matter is only loosely associated with sediment grains, and may readily be transformed from sedimentary to 'dissolved' organic matter.

C. Molecular Size Distribution of DOC

The molecular size distribution of DOC in anoxic pore water was determined using ultrafiltration techniques described earlier (see Chapter 2). Pore water from eight different cores was fractionated into various molecular weight (MW), ranges, and each fraction analyzed for DOC. The numerical results for the different fractions from all of these cores are tabulated in Appendix D. These data are reported in

the appendix as absolute DOC concentrations (mgC/l), for each fraction, and as the percentage each fraction contributes to the total (e.g. unfractionated pore water), DOC.

Figures 5-7 through 5-11 illustrate various MW fractions of DOC in pore water from four sites in Great Bay as functions of depth. These data are reported as percentages of the total DOC, rather than absolute concentrations, to allow a clearer picture of how the MW distributions change as functions of sample location and depth. One clear trend in these cores was the decrease in the average MW of the DOC in pore water in a direction toward the freshwater source. For example, in the <1,000 MW fraction (Figure 5-7), whole core averages ranged from 13.5% of the total DOC at Site 1, to 19.2% at Site 3, 21.5% at Site 4 and a large jump to 60.7% at Site 5. The significance of this trend is uncertain, however, it is possible that it may result from a difference in the nature of the organic matter at Site 5, compared to the other sampling locations. Alternatively, the mechanisms producing DOC at Site 5 (both biological and non-biological), may differ from those at the other sites. However, any differences in mechanism are not related to either temperature or salinity variations among the sites, since these were similar from location to location (see Chapter 4).

These results emphasize the importance of relatively high MW organic matter to the total DOC pool in Great Bay pore water, especially at Sites 1, 3 and 4. Krom and Sholkovitz (1977), observed a similar preponderance of high MW DOC in a single core from Loch Duich, Scotland. Of this high MW DOC in Great Bay pore water, the 50,000 to 1,000 MW fraction (Figure 5-8), was observed to predominate at Site 3 and

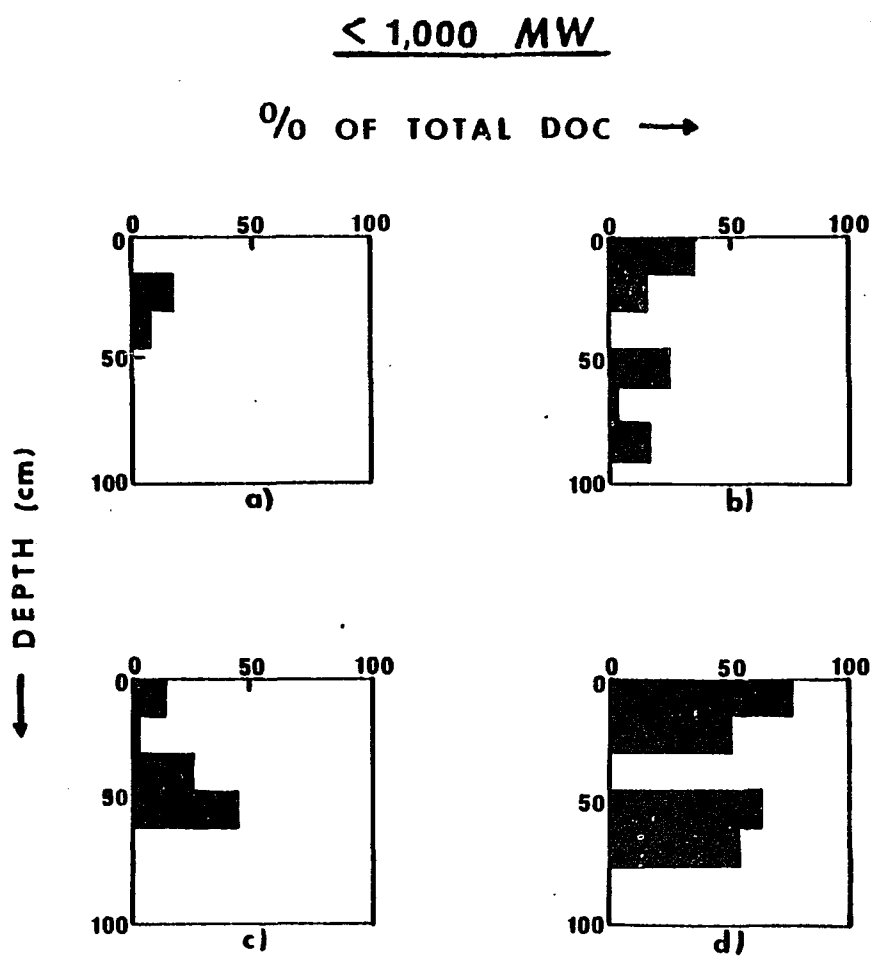

Figure 5-7. Percentages of total DOC <1,000 MW versus depth (cm), at four Great Bay sites: a) Site 1 (8-11-80); b) Site 3 (7-11-80); c) Site 4 (8-11-80); and d) Site 5 (7-11-80).

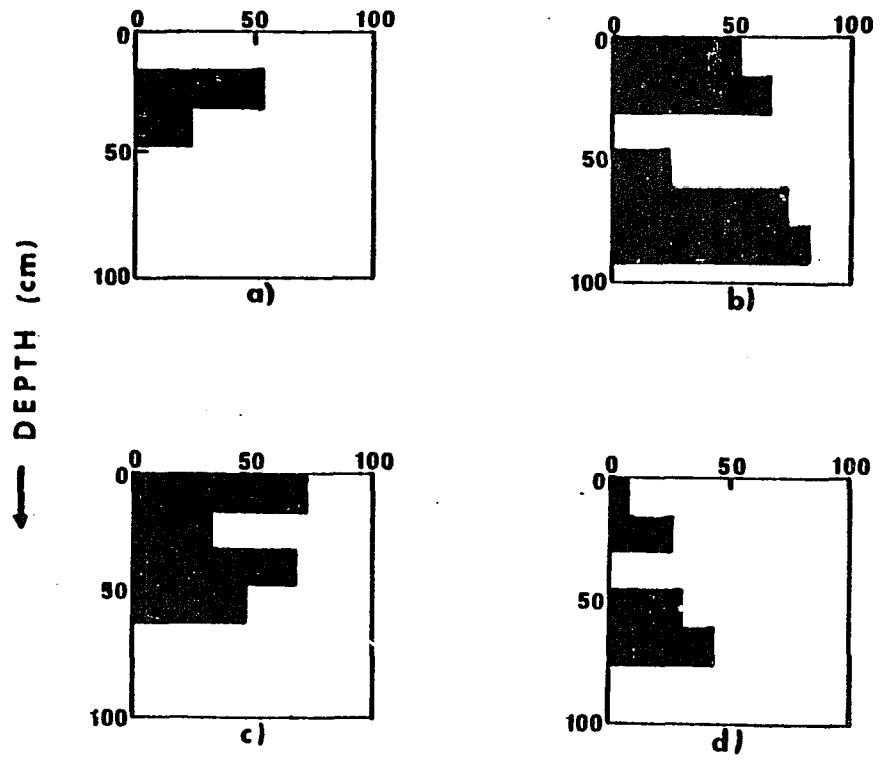

Figure 5-8. Percentages of total DOC 50,000 - 1,000 MW versus depth (cm), at four Great Bay Sites: a) Site 1 (8-11-80); b) Site 3 (7-11-80); c) Site 4 (8-11-80); and d) Site 5 (7-11-80).

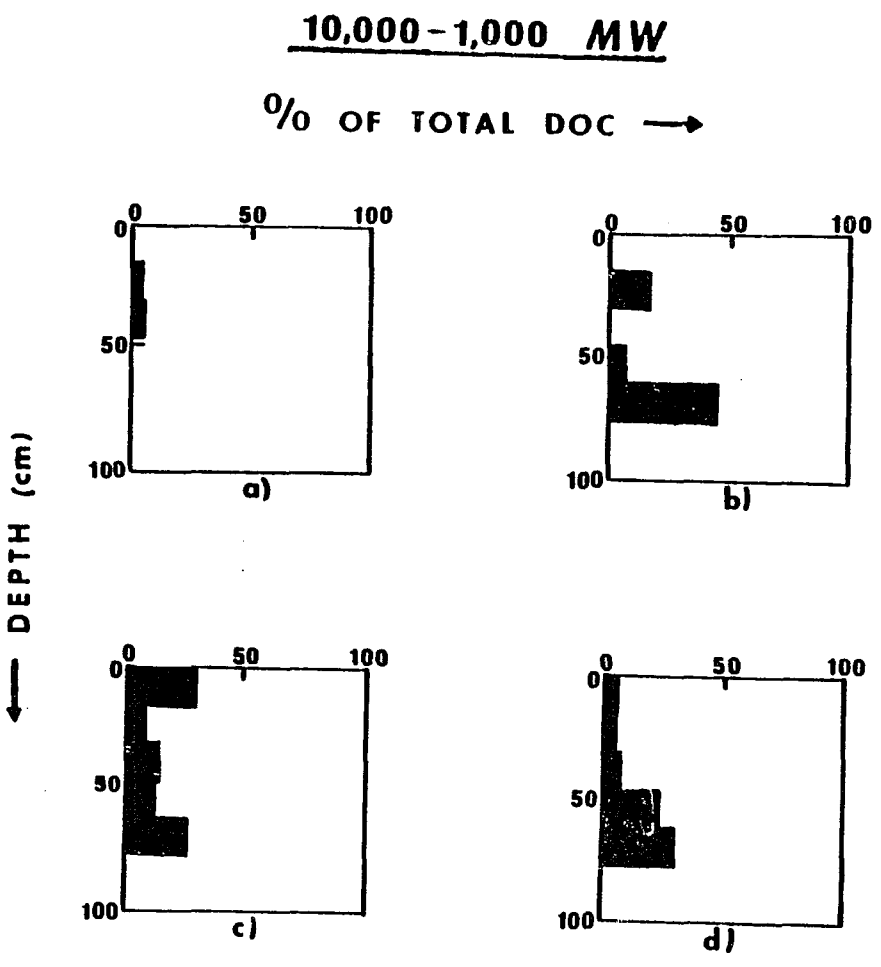

Figure 5-9. Percentages of total DOC 10,000 - 1,000 MW versus depth (cm) at four Great Bay sites: a) Site 1 (8-11-80); b) Site 3 (7-11-80); c) Site 4 (8-11-80); and d) Site 5 (7-11-80).

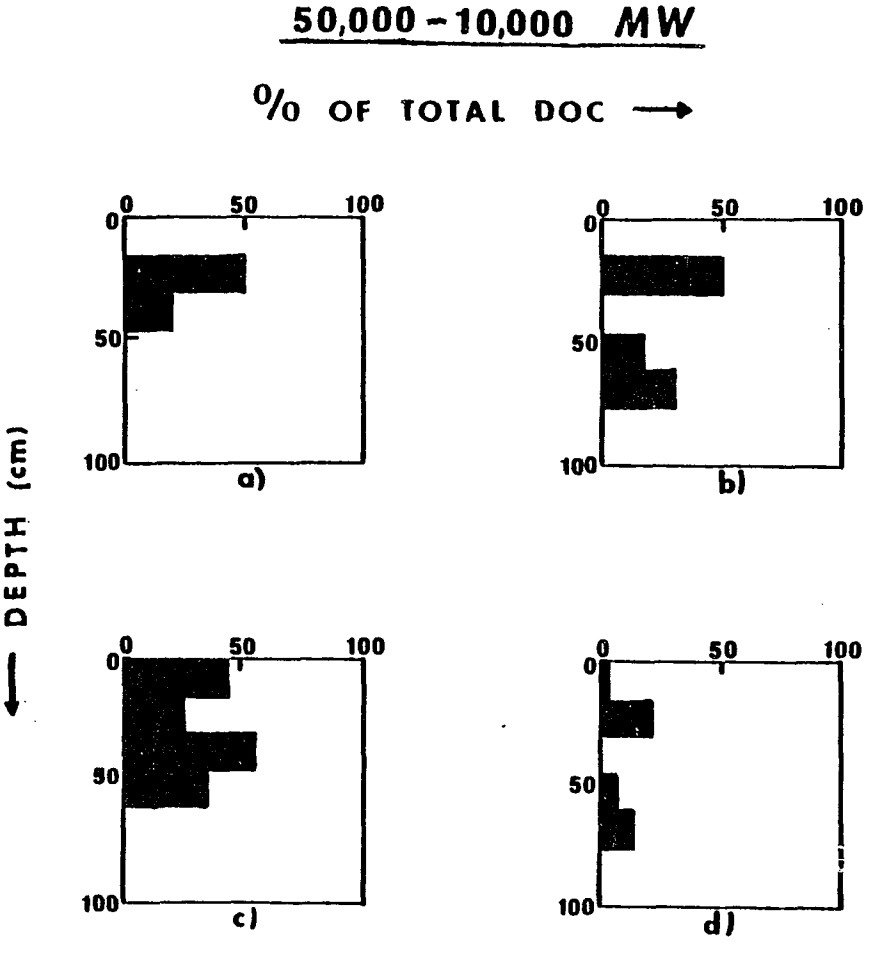

Figure 5-10. Percentages of total DOC 50,000 - 10,000 MW versus depth (cm) at four Great Bay sites: a) Site 1 (8-11-80); b) Site 3 (7-11-80); c) Site 4 (8-11-80); and d) Site 5 (7-11-80).

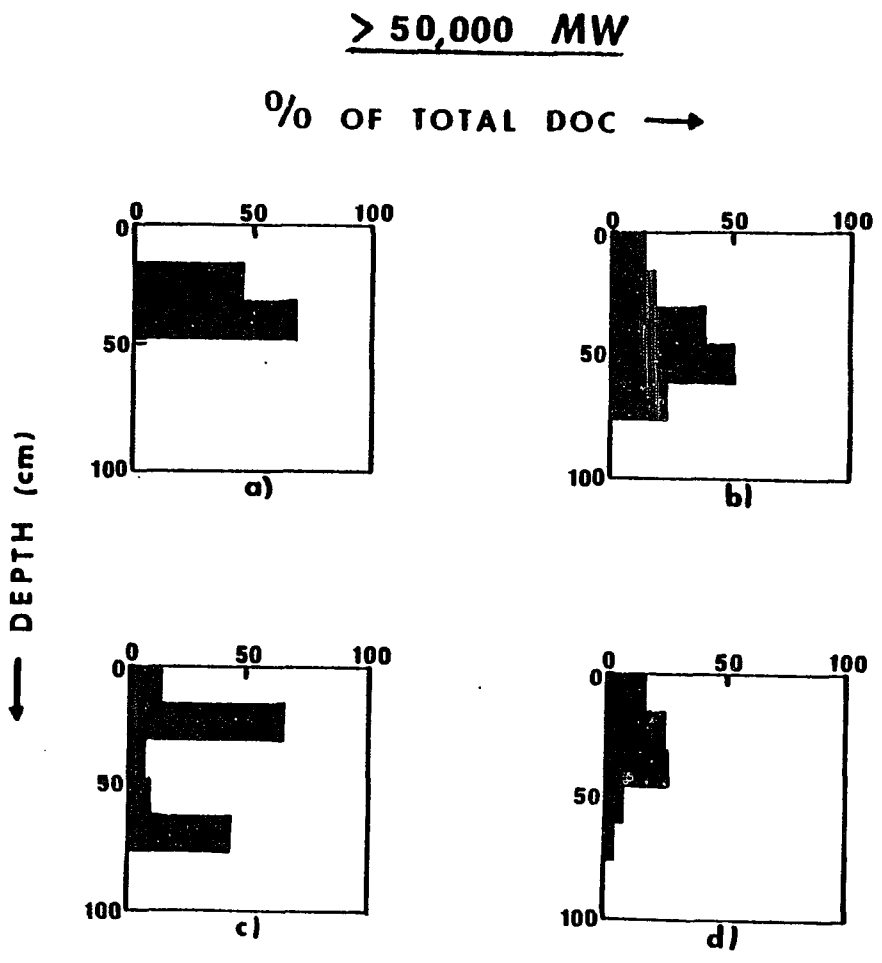

Figure 5-11. Percentages of total DOC >50,000 MW versus depth (cm), at four Great Bay sites: a) Site 1 (8-11-80); b) Site 3 (7-11-80); c) Site 4 (8-11-80); and d) Site 5 (7-11-80).

4 (59% and 55% of the total DOC, respectively, in whole core averages). At Site 5, 27% of the total DOC was in the 50,000 - 1,000 MW size class. Further fractionation of this size class into 10,000 to 1,000 and 50,000 to 10,000 MW ranges (Figures 5-9 and 5-10, respectively, indicated a predominance of the 10,000 to 1,000 size fraction at Sites 1 and 4; but a relatively even distribution of these two size classes at Sites 3 and 5. As mentioned above, the 50,000 MW fraction was the predominant class at Site 1, constituting up to 56% of the total DOC. This fraction gradually decreased in importance in a direction toward the freshwater source (opposite to the trend observed in the <1,000 MW fraction), to 24% of the total DOC at Site 3, 27% at Site 4 and 15% at Site 5.

In addition to lateral variations, the MW distribution of DOC with depth was also observed to change. In the cores from Sites 1, 3 and 5, the <1,000 MW fraction of the DOC diminished with depth as a percentage of the total DOC (Figure 5-7). This is similar to the results obtained by Krom and Sholkovitz (1977), and is consitent with their model of production of high MW dissolved organic matter (e.g. fulvic acid, humic acid, etc.), by polymerization or condensation of low MW DOC in anoxic marine sediments. The possible nature of these reactions has been previously discussed (Nissenbaum, 1974; Pocklington, 1977; and Templeton, 1980).

Increases in the high MW dissolved organic matter at Sites 3 and 5 were observed to be, primarily, in the 50,000 to 1,000 MW size range (Figure 5-8), with depth. However, at Site 1 the high MW DOC produced was predominantly >50,000 MW (see Figure 5-11). No consistent depth trends for the 50,000 to 10,000 MW or the 10,000 to

1,000 MW fractions were observed (Figures 5-10 and 5-9, respectively). The production of higher MW DOC (e.g. >50,000), at Site 1 compared to Sites 3 and 5 is consistent with the general decrease in whole core average DOC molecular weights in a direction toward the freshwater source, as discussed above.

One interesting depth trend in the Site 3 and 5 cores is the mid depth maximum exhibited by the >50,000 MW fraction (Figure 5-11). Mid depth maxima in the concentrations of a number of biochemically important organic species (e.g. amino acids, carbohydrates, etc.), in anoxic estuarine pore waters from Great Bay and elsewhere have also been observed (see Chapter 6). Thus, the mid depth maxima observed for the high MW DOC in these cores may be a result of the condensation of the large amounts of amino acids and carbohydrates found at these levels in the cores (i.e. melanoidon formation). The possible biochemical significance of the mid depth maxima for amino acids and carbohydrates observed in these cores is discussed in detail in Chapter 6.

The core from Site 4 (Footman Islands), showed a quite different DOC MW distribution with depth, than that observed at the other three sampling sites (Figures 5-7 through 5-11), displaying a rather irregular profile for most fractions. The reasons for this are unclear, but may simply be a result of lateral variability, since other cores from Site 4 (see discussion below), had depth trends similar to the other sampling sites.

A series of gravity cores were obtained from Site 4 (Footman Islands), in June, 1980, August, 1980 and April, 1980 to establish whether any seasonal change in the molecular weight distribution of DOC in estuarine pore water takes place. Since large seasonal changes in

the DOC concentrations of these cores were observed, presumably due to temperature induced solubility effects, changes in the DOC MW distribution were also expected. However, as illustrated in Figures 5-12 through 5-14, no such change was observed. Whole core average values for the various molecular weight fractions were: 28%, 23% and 15% for the >50,000 MW fraction; 57%, 55% and 61% for the 50,000 to 1,000 MW fraction; and 15%, 22% and 24% for the <1,000 MW fraction in the June, August and April cores, respectively. The dominance of the 50,000 to 1,000 MW fraction in these cores is in agreement with the molecular weight distribution of DOC discussed above. The June and April cores also exhibited similar depth profiles for the various DOC MW fractions. These depth profiles were characterized by increasing percentages of the 50,000 to 1,000 MW fraction with depth, and decreases in the amounts of DOC in the >50,000 and <1,000 MW fractions. This was in good agreement with the depth trends observed at Sites 3 and 5, as discussed above. The August core exhibited a rather different, irregular depth profile, probably due to lateral variability.

The above results indicate that although a substantial decrease in the concentration of DOC in these pore waters occurs between the summer and fall, the overall molecular weight distribution of the dissolved organic matter remains relatively unchanged. Thus, the mechanism responsible for the removal of DOC from the pore water during the fall is non-selective. This may imply the presence of an equilibrium between high and low MW DOC in the pore water, whence the removal of polymeric DOC from the pore water (possibly by termperature induced solubility effects), results in the condensation of low MW DOC until a new equilibrium is established. Alternatively, it may be that more than

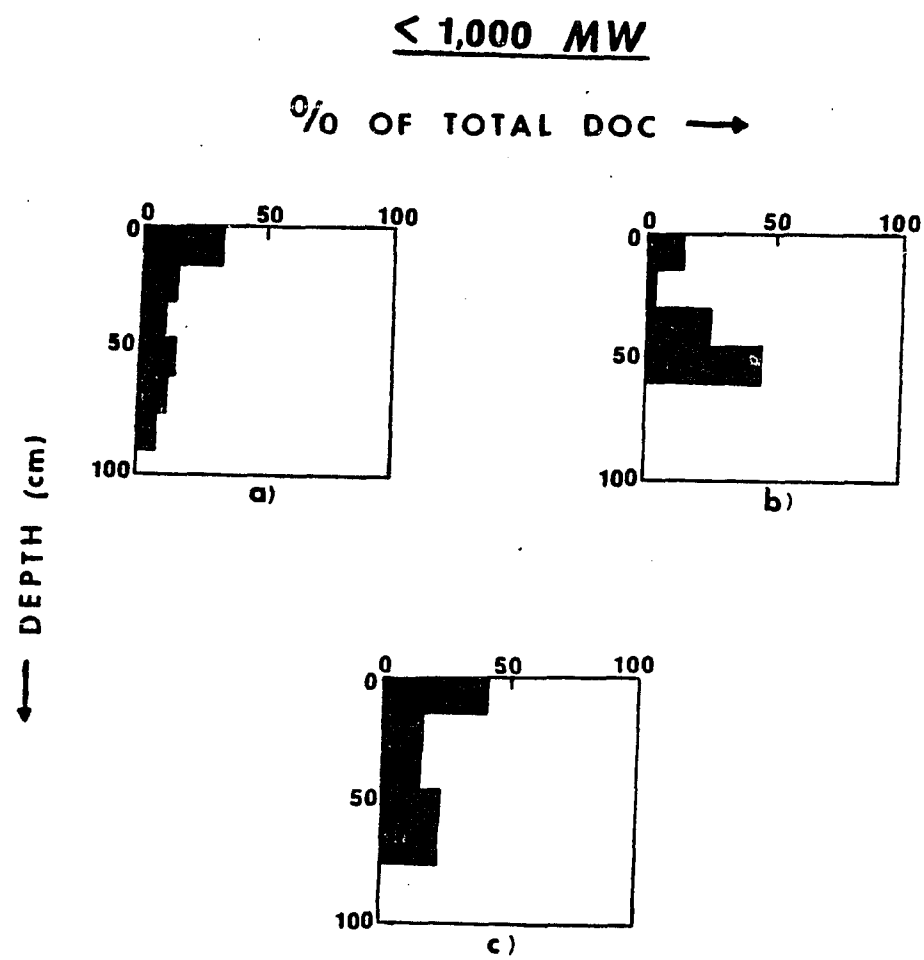

Figure 5-12. Percentages of total DOC <1,000 MW versus depth (cm), at Site 4: a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); and c) Core OAX-III (4-15-81).

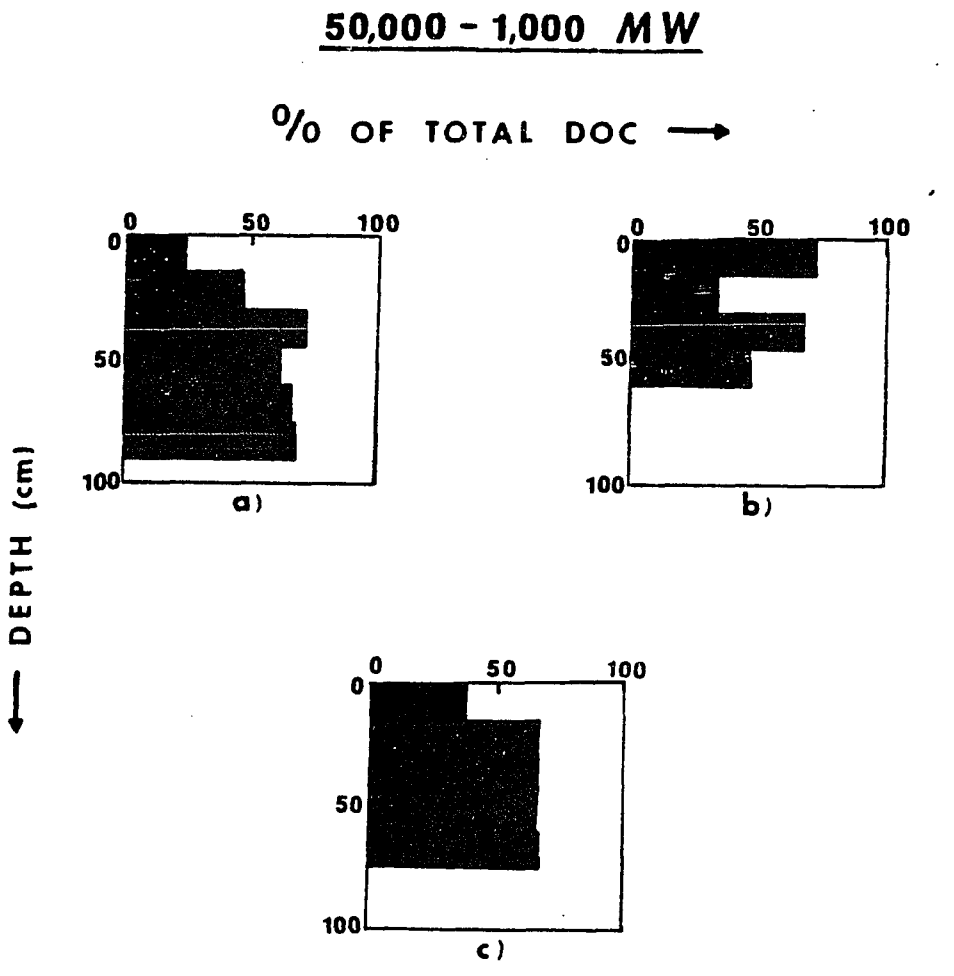

Figure 5-13. Percentages of total DOC 50,000 to 1,000 MW versus depth (cm), at Site 4: a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); and c) Core UF-III (4-15-81).

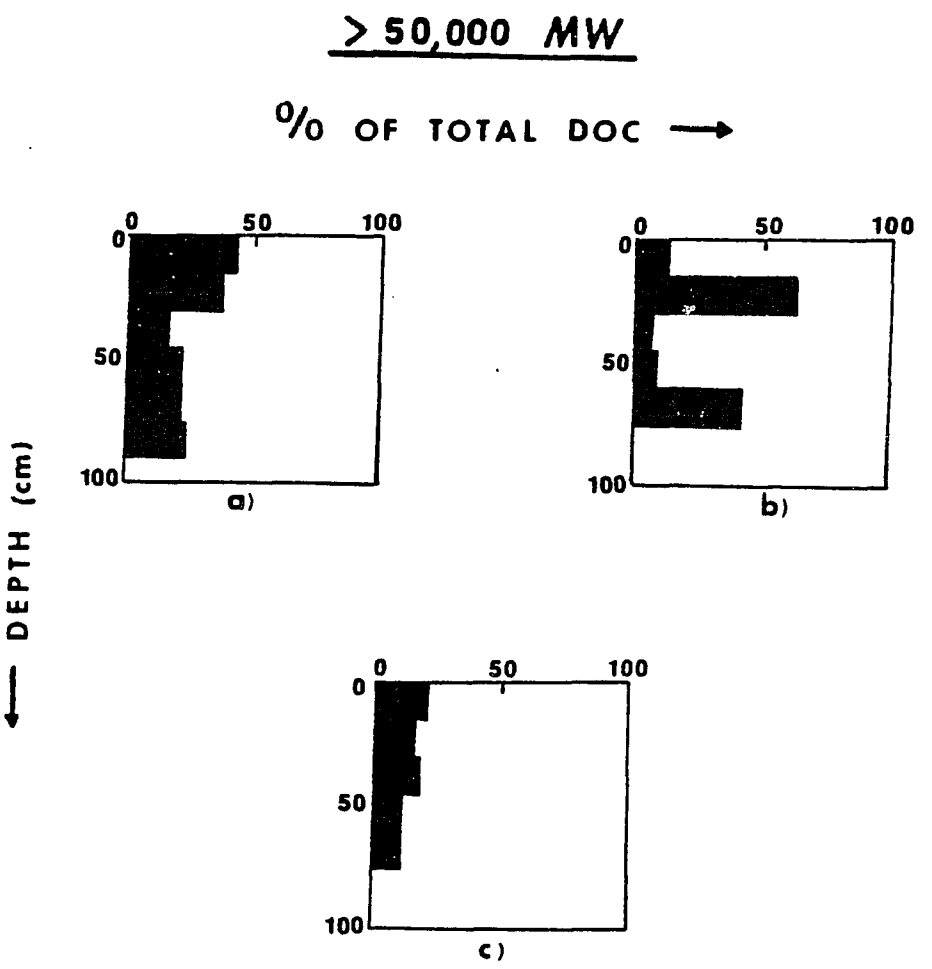

Figure 5-14. Percentages of total DOC >50,000 MW versus depth (cm), at Site 4: a) Core OAX-I (6-23-80); b) Core UF-VII (8-11-80); and c) Core OAX-III (4-15-81).

one process is involved in the seasonal regulation of DOC pore water concentrations, and the action of these processes, in concert, maintains the DOC MW distribution.

In addition to studies of the molecular weight distribution of DOC in pore waters from deep cores, the DOC MW distribution of pore waters from a number of box cores was also investigated. Whole core average values for the various MW fractions from these shallow cores were, in géneral, similar to those observed in the pore waters from the uppermost sections of the gravity cores. However, depth profiles of the various MW fractions of the DOC in these box cores were often very irregular, probably reflecting the effects of overlying water intrusion due to advective processes such as wave and tidal action and bioturbation.

III. Conclusions

In this chapter the results of a comprehensive survey of the distribution of dissolved organic carbon in pore waters from Great Bay, New Hampshire sediments were presented and discussed. These results have provided some useful insights into the process of early diagenesis of organic matter in nearshore marine sediments.

Concentrations of DOC in the pore waters were observed to reach values of between 10 and 100 times those in the overlying seawater. In addition, these concentrations were observed to increase with increasing depth in the sediments. These findings were in agreement with those of previous workers (Lindberg and Harriss, 1974; Krom and Sholkovitz, 1977; Lyons et al., 1979c; and Barcelona, 1980). This accumulation of DOC in anoxic pore waters is undoubtably the result of the bacterial degradation of detrital biopolymers deposited in the sediments. This process

produces more soluble, smaller organic compounds from large polymeric materials, and the slowness of diffusion allows the accumulation of this soluble organic material in pore waters. Although high concentrations of DOC were found in pore waters from all five Great Bay sampling sites, a positive correlation between DOC concentration and % sedimentary organic carbon was observed. Thus, higher concentrations of DOC were observed at Sites 4 and 5.

Concentrations of DOC were also observed to vary seasonally in both box and gravity cores. In shallow cores, the seasonal changes in DOC were linked to seasonal changes in heterotrophic bacterial activities and the burrowing activities of marine macrofauna (e.g. bioturbation). In fact, seasonal changes in the concentration of DOC in the pore waters of these cores closely paralleled those for titration alkalinity, ammonia, phosphate and total iron (see Figure 4-31). The large seasonal changes observed in the DOC concentrations of pore waters from the deep sections of gravity cores were unexpected, and presented a problem in explaining the removal of large amounts of DOC from these pore waters in the fall and winter. Since diffusion is too slow a process to account for the observed changes over such a short span of time, this seasonal trend was attributed to a temperature induced solubility effect. In this hypothesis, a large pool of colloidal organic matter exists in the sediments, and may dissolve in the pore water or precipitate from solution depending on the ambient temperature.

Studies of the molecular size distribution of DOC in Great Bay pore waters using ultrafiltration techniques have revealed the general colloidal nature of this material. In many of these cores, the 50,000 to 1,000 MW size class clearly dominated the DOC size distribution.

Whole core average size distribution of DOC were observed to become smaller in approaching the freshwater source of the estuary. Thus, at Site 5 in Great Bay the <1,000 MW size class was observed to predominate, while at Site 1 the >50,000 MW DOC dominated. In addition to this lateral trend in the size distribution of DOC, a vertical trend of increasing molecular size with increasing sediment depth was generally observed. This was in agreement with the findings of Krom and Sholkovitz (1977), for pore waters from a Scottish Loch, and may be a consequence of the condensation of small molecular weight compounds such as amino acids and carbohydrates. No seasonal change in the molecular weight distribution of DOC at Site 4 in Great Bay was observed, despite a large seasonal change in the concentration of DOC in the pore waters at this sampling site. This discrepancy was attributed to the existence of an equilibrium between high and low molecular weight organic matter in anoxic estuarine pore waters.

CHAPTER 6

ORGANIC MATTER IN ANOXIC PORE WATER FROM GREAT BAY, N.H.

I. Introduction to Problem

In this chapter, the results from a diverse set of studies on organic matter in anoxic pore water are presented. The purpose of these studies was to obtain an understanding of some of the characteristics of organic matter in anoxic marine pore waters. A detailed understanding of the characteristics of this material may provide important insights into the biogeochemical processes occurring in anoxic sediments. A dual approach was undertaken, involving the analysis of the bulk organic matter in the pore water as well as the determination of specific organic compounds. The advantages of this dual approach were outlined earlier (see Chapter 1). Bulk characteristics of the pore water organic matter presented here include the relative polarity as determined by HPLC, ultraviolet/visible absorption and fluorescence. In the preceeding chapter, the distribution and nominal molecular weight of a large fraction of the bulk organic matter in pore water (i.e. the DOC), was discussed. Specific organic compounds in Great Bay pore waters that were determined and will be discussed in this chapter include the free amino acids and monosaccharides.

Nissenbaum and co-workers (1972), were among the first to investigate some of the bulk characteristics of pore water organic matter. The ultraviolet/visible absorption spectra of pore water organic matter

from Saanich Inlet, British Columbia sediments obtained by these researchers were similar to those characteristic of humic substances. Gradual increases in absorbance from 750 to 390 nm, and very rapid increases below this wavelength were observed. A weak shoulder in these spectra between 275 and 265 nm was noted, similar to that observed in marine 'Gelbstoffe' (Kalle, 1966). Similar absorption spectra for pore water organic matter from Scottish estuarine and eastern equatorial Atlantic Ocean sediments have been obtained by Krom and Sholkovitz (1977), and Ewald (1979), respectively. Krom and Sholkovitz (1977), also presented data on E_3/E_4 and E_4/E_6 spectral ratios from their ultraviolet/visible absorption spectra. Their E_4/E_6 ratios had an overall mean value of about 10, close to that for fulvic acid (Schnitzer and Kahn, 1972). In general, these values were observed to increase with increasing sediment depth. However, there is some doubt as to whether this trend is indicative of increasing condensation and humification of the dissolved organic matter (Nissenbaum and Kaplan, 1972).

Ewald (1979), has observed the fluorescence spectrum of pore water from eastern equatorial Atlantic Ocean sediments at two excitation wavelengths: 250 and 370 nm. The fluorescence of the pore water excited at 250 nm exhibited two characteristic regions. One band was observed between 270 and 350 nm with a maximum at 300 nm. A second broad band with two distinct maxima at 415 and 440 nm was found between 350 and 600 nm. The fluorescence spectrum obtained at an excitation wavelength of 370 nm was well defined and very broad with a single maximum observed between 440 and 450 nm. This was similar to the fluorescence spectrum of fulvic acid extracted from the sediments. In

addition, the broad fluorescence band observed between 350 and 600 nm at an excitation wavelength of 250 nm was similar to that of humic acid extracted from the sediments.

These spectroscopic results tend to support the idea discussed earlier in Chapter 1, that humic substances in marine sediments are produced by condensation reactions occurring in the pore water. Infrared absorption spectra of pore water organic matter have also revealed patterns of absorption bands similar to those of humic and fulvic acids (Nissenbaum et al., 1972; and Krom and Sholkovitz, 1977). However, a possible criticism of all of these studies is that no precautions were taken to exclude oxygen during sample processing and spectroscopic analysis. As shown earlier (see Chapter 3), exposure of organic matter from anoxic marine pore water to atmospheric O_2 may result in structural changes in this material.

Only one previous study has been reported in which reversed phase high pressure liquid chromatography (HPLC), was used to fractionate pore water organic matter. Lammela (1981), observed 2 major fractions in a liquid chromatogram of pore water organic matter from Great Bay, N.H. sediments (Site 3), using a C-18 μ-Bondapak column and a mobile phase of 20% (V/V), n-propanol in water (flow rate = 1.5 ml/min.; ultraviolet/visible detection at 254 nm). Besides these two major fractions, a number of smaller peaks were observed at longer elution times. Lammela (1981), also fractionated organic matter extracted from anoxic marine sediments (distilled/deionized water and artificial seawater extractants), using reversed phase HPLC under the same conditions as describe above. As expected, the chromatograms of the sediment extracts were much more complex and significantly more non-polar than

those for the pore water. These results were only for pore water and extracted sedimentary organic matter in surficial sediments, and no information on depth or lateral variations were reported.

As mentioned previously in Chapter 1, a number of specific compounds have been determined in anoxic marine pore waters, including: amino acids (Stephens, 1963; Clark et al., 1972; Starikova and Korzhikova, 1972; Henrichs and Farrington, 1979; and Gardner and Hanson, 1979), carbonhydrates (Lyons et al., 1979c), low molecular weight fatty acids (Miller et al., 1979; and Barcelona, 1980), hydrocarbons (Nissenbaum et al., 1972), urea (Rosenfeld, 1981), and dissolved humic and fulvic acids (Nissenbaum et al., 1972; and Lyons et al., 1979c). However, with the possible exception of free amino acids, little is known about the distributions of these compounds in marine pore waters.

Carbohydrates have been observed to constitute up to 50% of the dissolved organic matter in the pore water of Bermuda carbonate sediments (Lyons et al., 1979c). This percentage was observed to decrease rapidly with increasing depth in the sediments, to values of about 2% at 60-70 cm. Free amino acid (Gardner and Hanson, 1979), and low molecular weight fatty acid pore water concentrations (Miller et al., 1979; and Barcelona, 1980), have also been observed to decrease with increasing depth in anoxic marine sediments. However, many pore water depth profiles of these organic compounds displayed curious subsurface concentration maxima at depths of 20 to 40 cm in the sediments. Low molecular weight fatty acids have also been observed to constitute a significant portion of the dissolved organic matter in marine pore waters (up to 50% of the DOC in one sample, Barcelona, 1980). However, free amino acids appear to compose a much smaller percentage of the

pore water organic matter, generally less than 2% (Henrichs and Farrington, 1979; and Gardner and Hanson, 1979). The overall decrease with depth in the concentrations of these biochemically active species in pore waters may be a result of two factors: 1) the utilization of these compounds by anaerobic bacteria in the sediments, and 2) the condensation of these compounds to form high molecular weight geopolymers in the sediments. These processes were discussed in some detail in Chapter 1, however, the significance of the subsurface concentration maxima of free amino acids and fatty acids in pore waters has not been addressed. The concentrations of all of these organic species in marine pore waters have generally been observed to be one to two orders of magnitude greater than those in the overlying seawater.

Henrichs and Farrington (1979), conducted a detailed survey of individual amino acids in marine pore waters. Glutamic acid was observed to be the predominant amino acid in these samples, with β-aminoglutaric acid (a non-protein amino acid), also found in high concentrations. Together, these two amino acids constituted from 76% to 90% of the total free amino acids in the pore waters of these sediments. Gardner and Hanson (1979), also observed large amounts of glutamic acid and an unknown amino acid (possibly β-aminoglutaric acid), in marine pore waters. However, these amino acids were not as predominant in these samples, and high concentrations of alanine, glycine and serine were also observed. The ubiquity of glutamic acid is interesting, since this amino acid is produced during transamination in the bacterial metabolism of amino acids (Henrichs and Farrington, 1979). β - Aminoglutaric acid may be formed by the bacterially mediated transformation of glutamic acid (Henrichs and Farrington, 1979). Surprisingly, the

individual amino acid distributions in marine pore waters and acid hydrolysates (6M HCl) of marine sediments showed little correspondence (Morris, 1975; Carter and Mitterer, 1978; and Henrichs and Farrington, 1979). Thus, bacterial proteolysis of detrital proteins is either highly selective, or the freed amino acids are further metabolized to produce the observed distributions. Nissenbaum and co-workers (1972), have investigated the individual amino acid spectrum of a high molecular weight organic polymer which they isolated from marine pore water. Alanine and glycine were the dominant amino acids in this polymer. However, large amounts of serine, glutamic acid, threonine, aspartic acid and valine were also found. This distribution corresponds, roughly, to the free amino acid distribution in marine pore waters observed by Gardner and Hanson (1979); and tends to support the amino acid/carbohydrate condensation model for the formation of sedimentary humic substances (Krom and Sholkovitz, 1977).

Formic, acetic and butyric acids have been observed to dominate the volatile fatty acid distribution in marine pore waters (Miller et al., 1979; and Barcelona, 1980). As discussed in Chapter 1, these fatty acids are extremely important metabolites for sulphate reducing bacteria, and their predominance in the pore water probably reflects this role. Nissenbaum and co-workers (1972), investigated the distribution of higher molecular weight fatty acids (i.e. C-14 to C-23 compounds); and observed the C-16 compound to predominate. This contrasted with their findings for n-paraffins in which the higher molecular weight compounds (i.e. those greater than C-22). Although these data must be considered preliminary, this result implies that if long-chain hydrocarbons are formed from the diagenetic transformation of fatty acids the process

does not just involve a simple decarboxylation (Cooper and Bray, 1963).

All sampling and sample handling procedures, as well as the analytical methodologies used to obtain the results presented in this chapter were discussed at length in Chapter 2. The optimization experiments for developing the HPLC mobile phase used in fractionating the pore water organic matter were also discussed in Chapter 2. Results from studies of the bulk properties of pore water organic matter are presented here first, followed by a discussion of free amino acids and monosaccharides in the pore water of Great Bay sediments.

II. Results and Discussions

A. Polarity of Pore Water Organic Matter

Reversed phase HPLC was used as a qualitative method for examining changes in the polarity of pore water organic matter with depth in the sediments and at different locations within the Great Bay estuary. Qualitative differences in the shapes of the liquid chromatograms, as well as differences in the number and retention times of various fractions were used as a measure of changes in the polarity of this material. A description of the instrumentation used and other aspects of the HPLC work was presented in Chapter 2. In all chromatograms presented here, an isocratic mobile phase of 60% water, 20% n-propanol and 20% acetonitrile at a flow rate of 4 ml/min was used.

Figure 6-1 presents a series of liquid chromatograms of pore water organic matter in a box core from Site 3 (Adams Cove), with each chromatogram representing pore water from a different depth in the sediments. In the 0-2 cm subsection of the core, three fractions are visible in the liquid chromatogram. The most polar fraction or first peak (note that polarity decreases from left to right in all of these

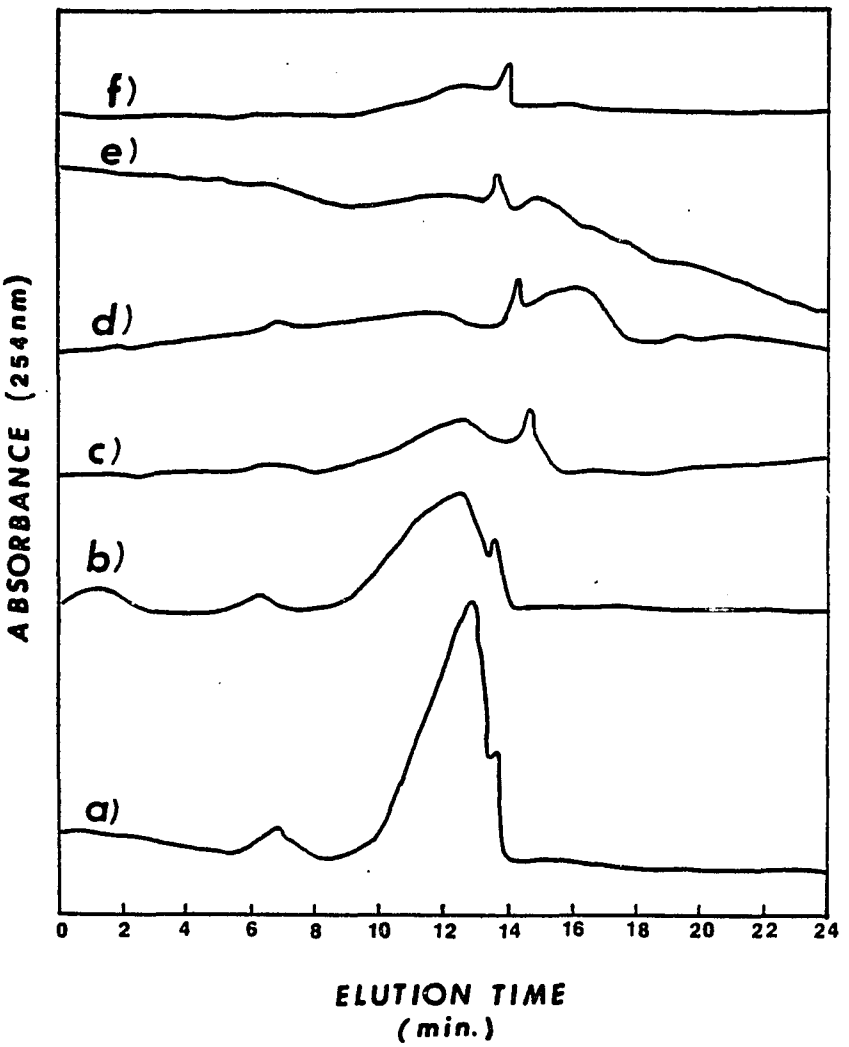

Figure 6-1. Reversed phase liquid chromatograms of pore water from Site 3 (11-14-80): a) 0-2 cm subsection; b) 2-4 cm subsection; c) 4-6 cm subsection; d) 6-8 cm subsection; e) 8-10 cm subsection; and f) 10-12 cm subsection. The mobile phase consisted of an isocratic mixture of 60% water, 20% n-propanol and 20% acetonitrile. The flow rate was 4 ml/min and the injection volume was 1.5 ml. For other conditions, see Chapter 2.

chromatograms), showed a gradual decline in ultraviolet/visible absorbance (254 nm), with depth, being totally absent in the 10-12 cm section of sediment. The second fraction apparent in the pore water from the 0-2 cm subsection also showed a gradual decline in absorbance with depth, although still present at a depth of 10-12 cm. These depth changes were not a result of decreases in the dissolved organic matter content of the pore water with depth, since DOC concentrations were observed to increase in this core over this vertical range (see Chapter 5, Figure 5-4 1). Fraction three in the 0-2 cm subsection, although showing a slight drop in absorbance between the first and second subsections of sediment, was visible in the liquid chromatograms of all the sediment subsections. In addition to the three fractions observed in the 0-2 cm subsection, other, less polar fractions were observed in deeper sections. These fractions were particularly evident in the 6-8 and 8-10 cm sediment sections. Overall, the polarity of the pore water organic matter in this core seemed to decrease with depth, as suggested by Nissenbaum et al. (1972).

There are two possible explanations for the overall lower absorbances of the chromatographic fractions with depth in the sediments, despite the higher DOC values deeper in the core: 1) the pore water organic matter in deeper sections of the sediment has a lower molar absorptivity as a result of diagenetic transformations, and 2) the homogeneity of this material decreases with depth, such that the absorbance of the organic matter is 'smoothed-out' over a broad range of the chromatogram. Previous workers have reported increased condensation of the pore water organic matter and higher absorbance of the whole pore water with depth in the sediments (Nissenbaum et al.,

1972; Krom and Sholkovitz, 1977; and Lyons and Gaudette, 1979). In addition, the ultraviolet/visible absorbance of the whole pore water in this study was observed to increase with depth. Thus, the second explanation is favored. The decreased homogeneity of the pore water organic matter with depth may be a result of both biological and chemical transformations of the originally deposited organic matter. Apparently, these transformations result in a myriad of endproducts with limited structural relationships to one another.

Reversed phase liquid chromatograms of pore water organic matter in gravity cores from Sites 4 (Footman Islands), and 5 (Squamscott River), are presented in Figures 6-2 and 6-3, respectively. For each core, chromatograms from four different depths are illustrated. Again, an isocratic mobile phase of 60% water, 20% n-propanol and 20% acetonitrile was used, at a flow rate of 4 ml/min for all chromatograms. All other conditions were as specified in Chapter 2.

The chromatograms from the two sampling sites were similar in a number of respects, although some qualitative differences were observed. In general, three fractions were observed in the chromatograms (indicated by the numbers 1, 2 and 3 in Figures 6-2 and 6-3), although fraction 1 is visible only in the deepest sediment section at Site 4. These three fractions were also observed in pore water from other Great Bay cores, when using a water/n-propanol/acetonitrile mobile phase (see Chapters 2 and 3). The chromatograms of the pore water from the 0-15 cm subsections in these gravity cores represent an average of the six chromatograms from the box core in Figure 6-1. In the Site 5 chromatograms (Figure 6-3), little or no qualitative changes with depth were observed. The increasing absorbances of all three fractions with sedi-

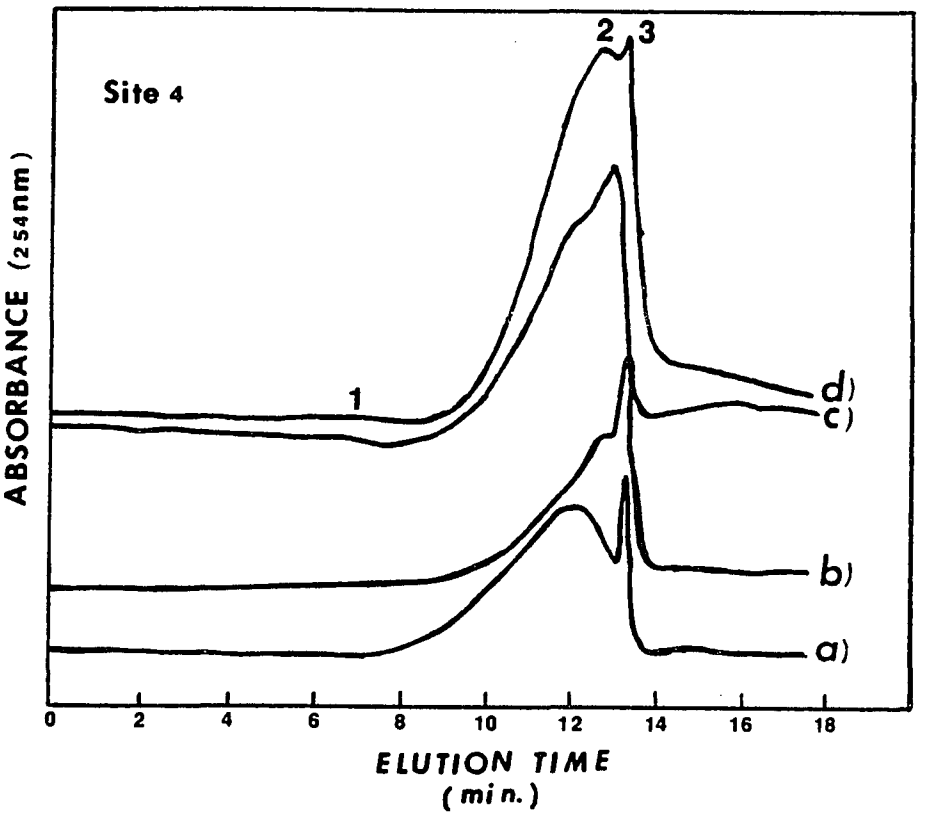

Figure 6-2. Reversed phase liquid chromatograms of pore water from Site 4 (5-8-81): a) 0-15 cm subsection; b) 15-30 cm subsection; c) 30-45 cm subsection; and d) 45-60 cm subsection. Conditions used were the same as described in Figure 6-1 and Chapter 2.

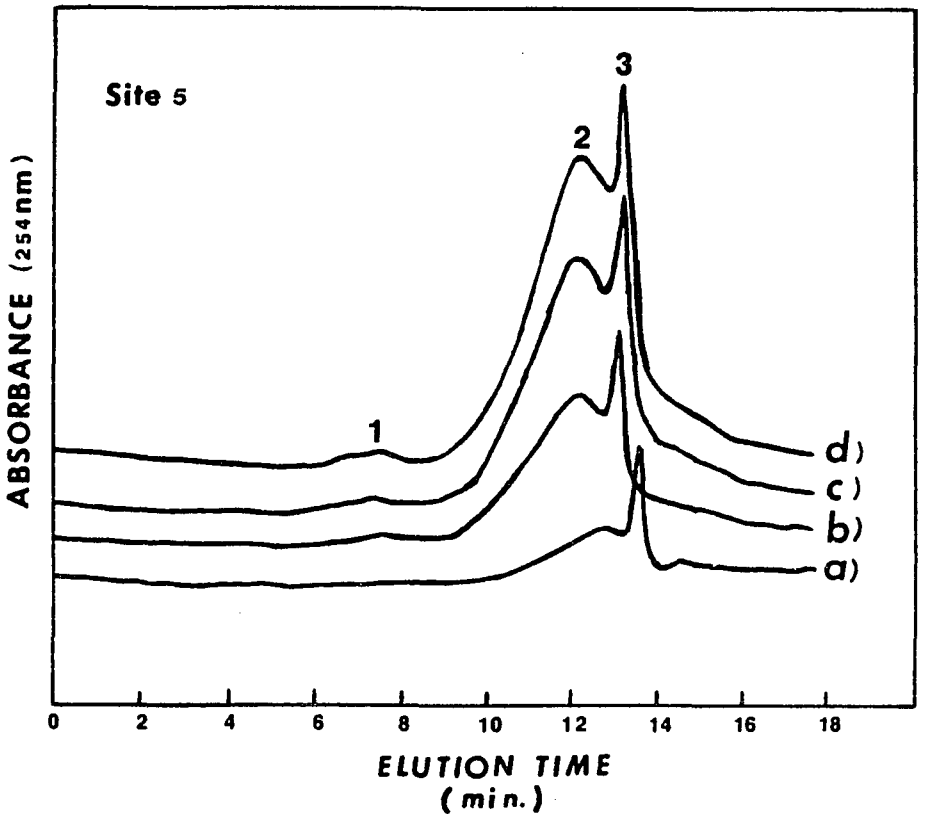

Figure 6-3. Reversed phase liquid chromatograms of pore water from Site 5 (5-8-81): a) 0-15 cm subsection; b) 15-30 cm subsection; c) 30-45 cm subsection; and d) 45-60 cm subsection. Conditions used were the same as described in Figure 6-1 and Chapter 2.

ment depth simply reflected the same trend in DOC. In the chromatograms from Site 4 (Figure 6-2), some qualitative changes in resolution with depth were observed. In the 0-15 cm subsection at this sampling location fractions 2 and 3 were observed to be quite discrete. However, the resolution of these two fractions decreased steadily with depth. This effect may, again, be due to chemical and biological transformations and a 'smoothing-out' of the chromatogram. This same effect was observed in the chromatograms of the pore water from the box core taken at Site 3 (Figure 6-1). Indeed, the 'smoothing-out' effect was more pronounced in the box core over a shorter depth range, indicating that the processes responsible for this effect are more rapid in the surficial sediments. This would be consistent with a microbial effect.

The qualitative differences observed between the chromatograms from Sites 4 and 5 probably reflect differences in the nature of the source organic matter at the two sites. Indeed, the virtual absence of fraction 1 in the chromatograms from Site 4 may reflect the overall greater molecular size of the pore water organic matter at this site compared to Site 5 (see Chapter 5). In addition, the lack of a 'smoothing-out' effect in the Site 5 chromatograms may indicate a greater resistance of the organic matter at this location to biological transformations.

B. Ultraviolet/Visible Spectroscopy

Ultraviolet/visible absorption spectroscopy (UV/Vis), of whole pore water organic matter and of fractions of this material separated by HPLC was carried out using a procedure outlined in Chapter 2. Absorption spectra of the whole pore water organic matter, scanned from 700 to 220 nm, for gravity cores from Sites 4 (Footman Islands), and 5

(Squamscott River), are presented in Figures 6-4 and 6-5, respectively. Absorbance was measured from 0 to 2, full scale for these samples. These spectra are virtually featureless, except for weak shoulders in the pore water from the 0-15 cm subsections at both sampling locations. This shoulder was much more pronounced in the gravity core from Site 5, extending from about 330 to 265 nm. These types of featureless UV/Vis spectra, with gradually increasing absorbance from 700 to 390 nm and rapidly increasing absorbance below this wavelength are characteristic of humic substances (Schnitzer and Kahn, 1972). As mentioned earlier, previous workers have observed similar UV/Vis spectra for pore water organic matter (Nissenbaum et al., 1972; Krom and Sholkovitz, 1977; and Ewald, 1979). However, the shoulder observed in the pore water from the top 15 cm of sediment in this study was considerably broader than those previously observed. It is not known whether this difference is due to environmental variability or to the fact that previous researchers failed to maintain anoxic conditions during sample handling and spectroscopic measurement.

The ratio of optical densities or extinctions at 350 and 465 nm (i.e. the E_3/E_4 ratio), and 465 and 665 nm (i.e. the E_4/E_6 ratio), have often been used to characterize humic substances and other naturally occurring organic matter (Schnitzer and Kahn, 1972). These ratios for the two gravity cores discussed above (e.g. from the UV/Vis spectra in Figures 6-4 and 6-5), are presented in Table 6-1. These two sampling sites had very similar values of E_3/E_4 and E_4/E_6. These values were intermediate between those observed by Krom and Sholkovitz (1977), for pore water from Scottish Loch sediments (overall mean value of 10.4), and those observed by Lyons and co-workers (1979c), in pore water from

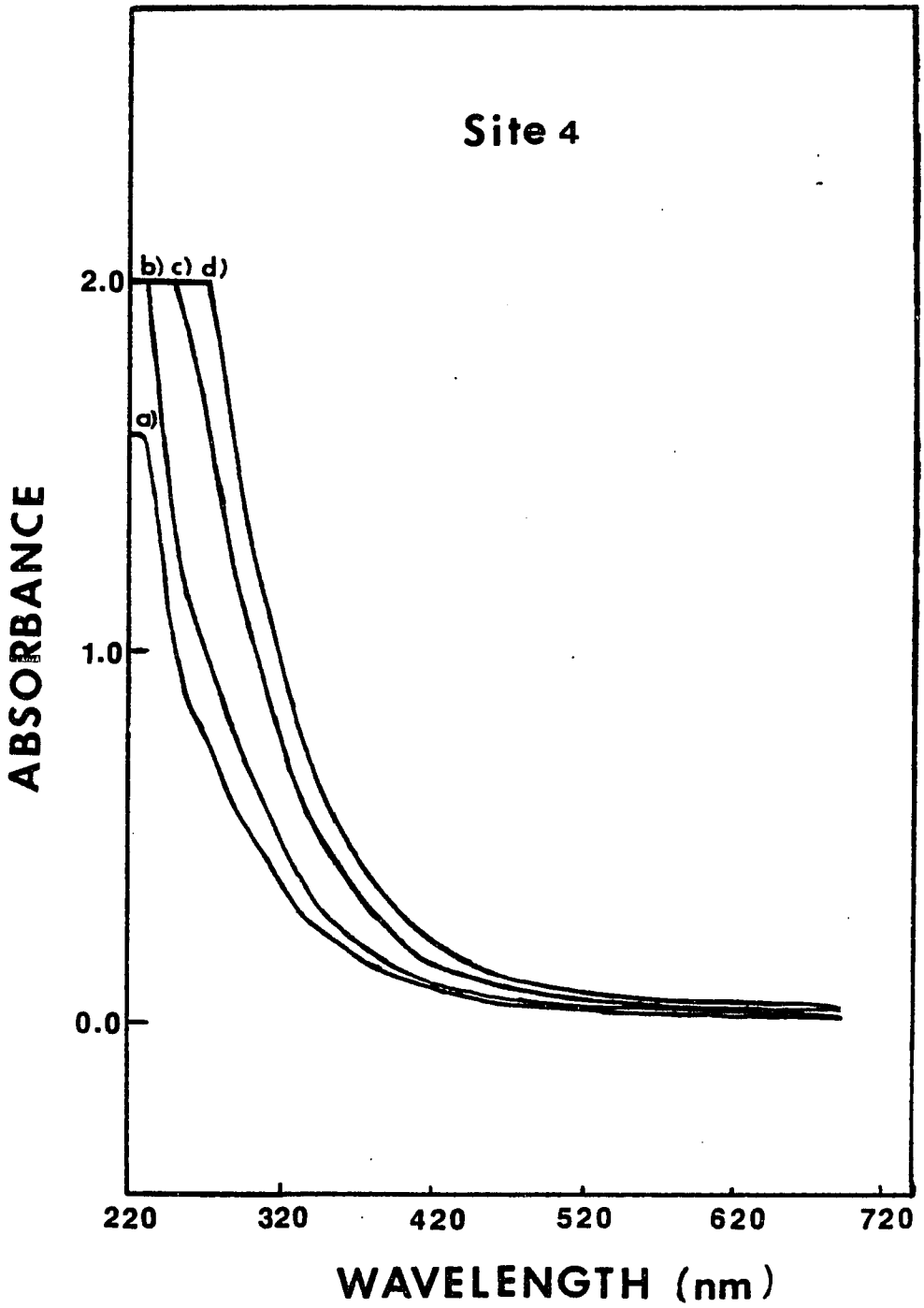

Figure 6-4. Continuous ultraviolet/visible absorption spectra of pore water from Site 4 (5-8-81). Procedure details were presented in Chapter 2. Each spectra represents the absorbance of pore water from different sediment depths: a) 0-15 cm; b) 15-30 cm; c) 30-45 cm; and d) 45-60 cm.

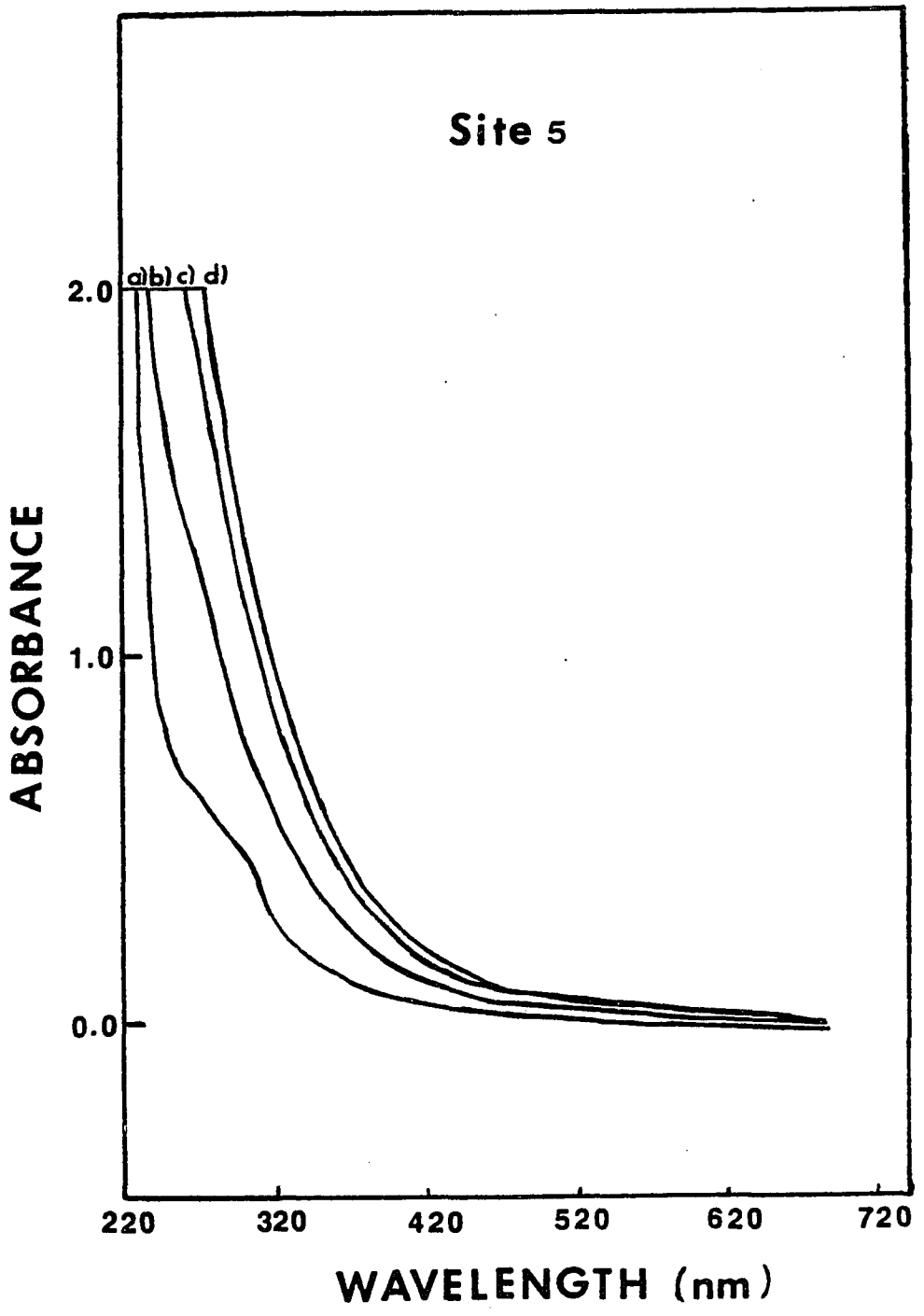

Figure 6-5. Continuous ultraviolet/visible absorption spectra of pore water from Site 5 (5-8-81). Procedural details were presented in Chapter 2. Each spectra represents the absorbance of pore water from different sediment depths: a) 0-15 cm; b) 15-30 cm; c) 30-45 cm; and d) 45-60 cm.

Table 6-1. Spectral ratios, E_3/E_4 and E_4/E_6 versus depth (cm), for pore water from gravity cores at Site 4 (Footman Islands), and Site 5 (Squamscott River).

Core FI-1
Site 4 (Footman Islands)
Date: 5-8-81

Depth (cm)	E_3/E_4	E_4/E_6
0-15	3.78	1.80
15-30	4.82	3.32
30-45	4.53	3.11
45-60	5.07	3.33
60-75	5.83	4.00
75-90	5.81	3.92

Core SQ-1
Site 5 (Squamscott River)
Date: 5-8-81

Depth (cm)	E_3/E_4	E_4/E_6
0-15	3.71	2.33
15-30	4.29	3.00
30-45	4.59	3.55
45-60	4.72	3.79
60-75	4.97	3.69
75-90	5.52	3.51

Bermuda carbonate sediments (overall mean value of 1.9). Lyons et al. (1979c), attributed the difference between their E_4/E_6 values and those of Krom and Sholkovitz (1977), to discrepant sources of organic matter between Scotland and Bermuda. However, based on this assertion the values from this study should be closer to those from Scotland (both of these areas are in nearshore clastic sediments, with large inputs of terrestrial organic matter), whereas the reverse is true. It is possible that the high values observed by Krom and Sholkovitz (1977), are a result of oxidation of the pore water organic matter, since no precautions to exclude oxygen were taken in their study. In the study by Lyons et al. (1979c), and in this work, special precautions were taken to exclude oxygen during sample handling and spectroscopic analysis.

Both the E_3/E_4 and E_4/E_6 ratios from this study were observed to increase with depth in the sediments, for pore water from both gravity cores (see Table 6-1). Similar trends for pore water organic matter were observed by Krom and Sholkovitz (1977), and Lyons et al. (1979c). In soils, a decrease in the E_4/E_6 ratio is indicative of increased aromaticity or condensation of the organic matter (Schnitzer and Kahn, 1972). However, Nissenbaum and Kaplan (1972), found no direct correlation between the degree of condensation of sedimentary humic substances and E_4/E_6 ratios. Thus, the trend of increasing E_4/E_6 of pore water organic matter with depth in the sediments is not necessarily an indication of decreasing aromaticity with depth.

In addition to UV/Vis spectroscopic studies of the whole pore water, the three major fractions observed in the liquid chromatograms of anoxic pore water from Great Bay sediments were collected individually from the chromatographic effluent and subjected to UV/Vis spectro-

scopic analysis. The samples were collected and analyzed under an atmosphere of N_2 gas at all times in order to avoid oxidation problems. The details of the procedures used were outlined in Chapter 2. The main objective of this study was to see if the separation of pore water organic matter into fractions by HPLC might increase the usefullness of the UV/Vis spectra. The fractions collected for spectroscopic analysis were those indicated in the liquid chromatograms in Figures 6-2 and 6-3: fraction 1 was collected over an elution time of 6.5 to 8.0 min., fraction 2 from 10 to 12.5 min., and fraction 3 from 12.5 to 13.5 min. Unfortunately, the spectra obtained for all three of these fractions at four different depths (0-15 cm, 15-30 cm, 30-45 cm, and 45-60 cm), from Sites 4 and 5 were entirely analogous to the spectra of the whole pore water, with the exception that the shoulder in these spectra extending from 330 to 265 nm was perhaps more pronounced. This was a disappointing result, although not totally unexpected, considering that each fraction in the liquid chromatogram still represents a mixture of many different compounds. This result does emphasize that these separate fractions are not grossly different in chemical structure.

C. Fluorescence Spectroscopy

Fluorescence spectra of pore water organic matter from Sites 4 and 5 in the Great Bay Estuary were obtained at three different excitation wavelengths: 250 nm, 264 nm, and 370 nm. The 250 nm and 370 nm wavelengths were chosen based on the work of Ewald (1979), who observed maximum fluorescence of pore water from pelagic Atlantic Ocean sediments at these two wavelengths. The 264 nm excitation wavelength was used because of a shoulder observed in the continuous UV/Vis spectra of pore water organic matter from Great Bay sediments in the region (see

Figures (6-4 and 6-5). Fluorescence emission at all of these excitation wavelengths was continuously scanned from 220 to 780 nm. All other operational procedures used to obtain fluorescence spectra were discussed in Chapter 2.

The fluorescence spectra obtained at excitations of 250 nm, 264 nm and 370 nm are presented in Figures 6-6, 6-7 and 6-8, respectively. In each figure, fluorescence spectra of pore water organic matter from two different depths each at Sites 4 and 5 in Great Bay (0-15 cm and 30-45 cm), are presented. Since different sensitivities on the fluorometer were used for each sample in order to keep the spectra on scale, the relationship of one spectrum to another is indicated by a multiplier factor next to each spectrum.

The fluorescence spectra at excitation wavelengths of 250 and 264 nm were characterized by a broad envelope extending from about 280 nm to 600 nm. In the spectra excited at 250 nm, two fluorescence maxima were visible in the spectra: one a shoulder at a wavelength range of 390 nm to 400 nm, and a second maximum at a wavelength range of 410 nm to 425 nm. The shoulders observable in these spectra at wavelengths of about 500 nm are due to Rayleigh Scattering. Ewald (1979), observed a somewhat different fluorescence spectrum for pore water excited at 250 nm, with two characteristic regions evident. One region extended from 270 nm to 350 nm, with a single maximum at around 300 nm. No such band was observed in the fluorescence spectrum of Great Bay pore water, although the broad band in these spectra extended somewhat into this region. Ewald (1979), observed a second broad band for his samples, which extended from 350 nm to 600 nm. This broad band exhibited two distinct maxima, at 415 nm and 440 nm. The qualitative

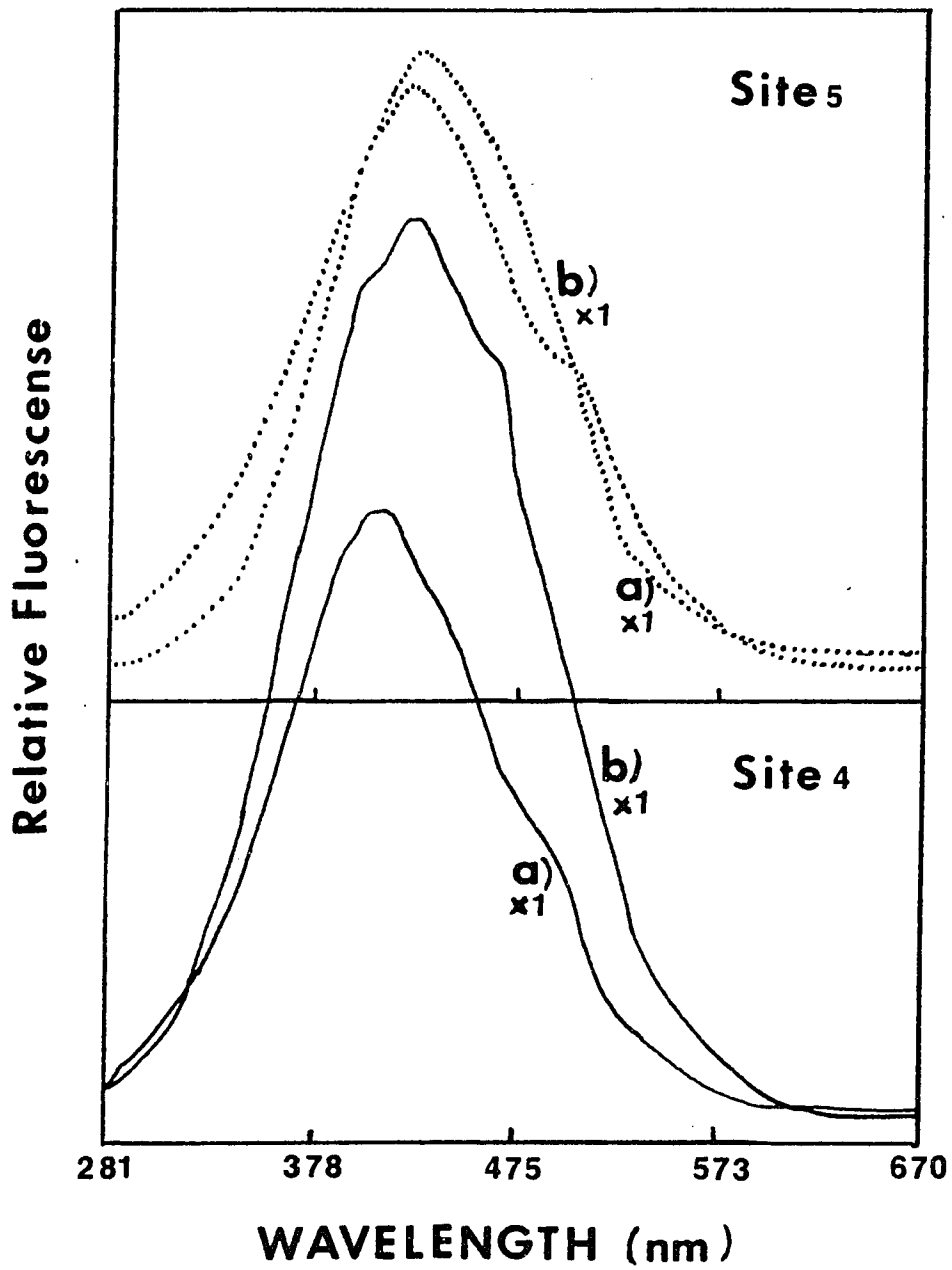

Figure 6-6. Fluorescence spectra of pore water organic matter from Sites 4 and 5 in Great Bay: a) 0-15 cm sediment subsection; and b) 30-45 cm sediment subsection. Excitation wavelength was 250 nm. The cores from Sites 4 and 5 were obtained on 5-8-81.

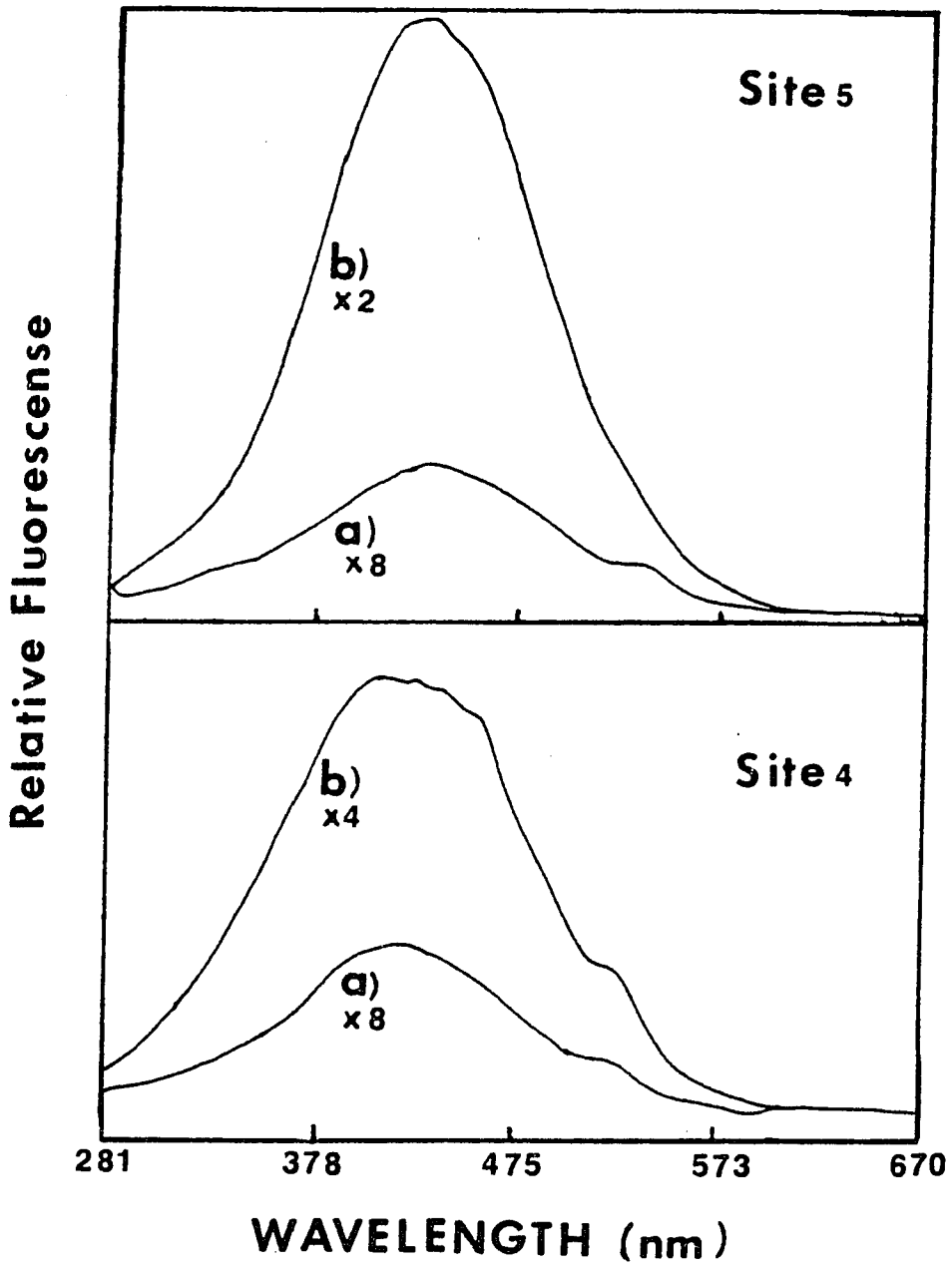

Figure 6-7. Fluorescence spectra of pore water organic matter from Sites 4 and 5 in Great Bay: a) 0-15 cm sediment subsection; and b) 30-45 cm sediment subsection. Excitation wavelength was 264 nm. The cores from Sites 4 and 5 were obtained 5-8-81.

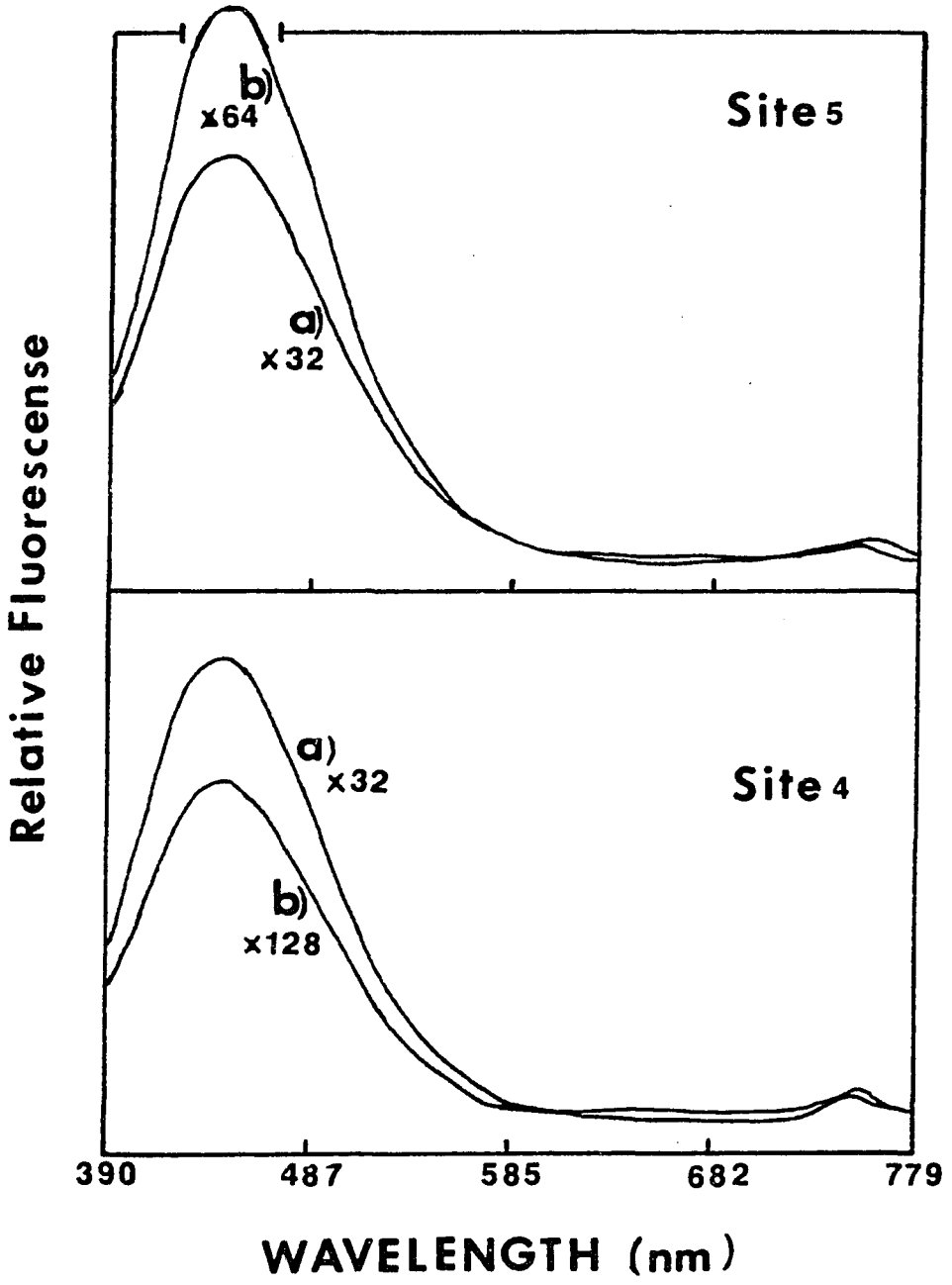

Figure 6-8. Fluorescence spectra of pore water organic matter from Sites 4 and 5 in Great Bay: a) 0-15 cm sediment subsection; and b) 30-45 cm sediment subsection. Excitation was at 370 nm. The cores from Sites 4 and 5 were obtained on 5-8-81.

differences between the fluorescence spectra observed by Ewald (1979), and those from this study at an excitation wavelength of 250 nm are difficult to explain, although it is possible that they reflect dissimilarities in the nature of the organic matter in the pore waters from Atlantic pelagic sediments and Great Bay sediments. The samples obtained by Ewald (1979), were from surface sediments and, although not stated in the article, were presumably oxic sediments. Since Great Bay sediments are anoxic below 6 cm in the sediments even in the winter months, the organic matter in Great Bay pore waters might be expected to have less functionality and be more condensed in structure (i.e. less polar). This could result in quite different fluorescence spectra between the two locations.

As mentioned above, the fluorescence spectra of Great Bay pore water at an excitation wavelength of 264 nm (Figure 6-7), were very similar to the spectra obtained by excitation at 250 nm (Figure 6-6). However, the broad fluorescence envelope observed in the 264 nm spectra (extending from about 280 nm to 600 nm), showed considerably less structure than the spectra excited at 250 nm. The shoulders observed in the spectra in Figure 6-7 at wavelengths of about 528 nm are, again, due to Rayleigh Scattering.

At an excitation wavelength of 370 nm, the fluorescence spectra of pore water organic matter observed in this study (Figure 6-8), were similar to those observed by Ewald (1979). A broad fluorescence envelope extending from about 390 nm to 580 nm with a single maximum at 446 nm was noted. This type of fluorescence spectrum is similar to that observed by Ewald (1979), for fulvic acid extracted from pelagic marine sediments. The small peaks in the fluorescence spectra in Figure 6-8 at

a wavelength of 740 nm to 750 nm are due to Rayleigh Scattering.

The relative fluorescence intensities of the pore water organic matter from Sites 4 and 5 in Great Bay were calculated from the peak heights of the major fluorescence peaks at each excitation wavelength (i.e. 250 nm, 264 nm and 370 nm). These values were normalized relative to a value of 100 established for the 30 cm to 45 cm subsection from Site 4, at an excitation wavelength of 370 nm. These results are presented in Table 6-2. Much greater fluorescence intensities in all samples were observed at an excitation wavelength of 370 nm than at either 250 nm or 264 nm. This may be indicative of a primarily substituted aromatic structure for the fluorescent organic matter in Great Bay pore waters (Becker, 1969). Fluorescence intensities at an excitation wavelength of 370 nm were observed to increase with depth. This effect is probably a result of three factors: 1) increasing total pore water organic matter with depth in the sediments, 2) increasing aromaticity of the organic matter due to condensation reactions, and 3) decreasing functionality of the organic matter. Fluorescence intensities at excitation wavelengths of 250 and 264 nm were also observed to increase with depth to 45 cm. However, below this level in the sediments, the intensity of fluorescence was observed to decrease at both of these wavelengths. This is probably indicative of some changes in the nature of the organic compounds in the pore water below 45 cm, but the kind of changes involved are uncertain from these data.

In addition to the fluorescence studies of the whole pore water organic matter discussed above, fractions of the organic matter from Great Bay pore waters separated by HPLC were also analyzed using fluorescence spectroscopy. Fractions 1, 2 and 3 of the pore water organic

Table 6-2. Relative fluorescence intensities of pore water organic matter at Sites 4 and 5.

Sample	Relative Fluorescence[a] A[b]	B[c]	C[d]
Site 4 (Footman Islands)			
1) 0-15 cm	1.4	3.1	34
2) 30-45 cm	2.1	3.9	100
3) 75-90 cm	1.7	3.8	146
Site 3 (Squamscott River)			
1) 0-15 cm	1.3	1.9	30
2) 30-45 cm	1.4	2.7	82
3) 75-90 cm	0.6	1.2	95

a) Units arbitrary and relative to a value of 100 established for the 30-45 cm sample from Site 4.

b) A = excitation 250 nm; emission 420-427 nm.

c) B = excitation 264 nm; emission 415-433 nm.

d) C = excitation 370 nm; emission 445-451 nm.

matter (see Figures 6-2 and 6-3), from various depths at Sites 4 and 5 in Great Bay were collected from the HPLC effluent and analyzed fluorometrically. Both the fraction collection process and the fluorescence analysis were conducted under nitrogen to avoid oxidation artifacts (see Chapter 3). All other fluorescence conditions were exactly the same as those used in the analysis of the whole pore water organic matter, discussed above. Fluorescence excitation of the fractionated pore water organic matter was carried out at the same three wavelengths as that for the whole pore water organic matter (i.e. 250 nm, 264 nm and 370 nm). The aim of this study was to ascertain if fractionation of pore water organic matter would result in any further structure in the fluorescence spectra of this material. Unfortunately, as with the UV/Vis absorption study of the fractionated organic matter from Great Bay pore waters, no further detail in the fluorescence spectra of this material was attained following fractionation. Again, this result emphasizes the relative structural similarity of these different fractions, and the insensitivity of UV/Vis absorption and fluorescence spectroscopy to whatever structural differences do exist among these different fractions.

D. Specific Organic Compounds in Anoxic Pore Water

Primary Amino Nitrogen. The concentrations of dissolved free amino acids (reported as primary amino nitrogen or PAN), and monosaccharides were determined in anoxic pore waters from a number of Great Bay cores. The results for PAN are presented in Table 6-3. In addition to the cores from Great Bay, concentrations of PAN in pore waters from Bermuda carbonate sediments (samples collected by Lyons, Gaudette and co-workers in June, 1978), are also presented in this table for

Table 6-3. Concentrations of primary amino nitrogen (gN/l), in pore water from Great Bay clastic and Bermuda carbonate sediments.

Great Bay Pore Water

Core A
Site 3 (Adams Cove)
2-10-78

Depth (cm)	µg PAN[1]/l
0-2	-
2-4	39.7
4-6	50.0
6-8	49.3

Core B
Site 5 (Squamscott River)
5-25-78

Depth (cm)	µg PAN[1]l
0-2	42.0
2-4	34.4
4-6	47.3
6-8	83.1

Core PS-I
Site 2 (Welsh Cove)
6-10-78

Depth (cm)	µg PAN[1]/l
0-5	14.5
5-10	19.2
10-15	20.5
15-20	43.7
20-25	40.8
25-30	53.4
30-35	50.9
35-40	44.3
40-45	49.7
45-55	35.3
55-65	25.2

Core PS-II
Site 4 (Footman Islands)
6-30-78

Depth (cm)	µg PAN[1]/l
0-5	214.3
5-10	152.2
10-20	101.6
20-30	76.7
30-40	82.0
40-50	156.7
50-60	180.8
60-70	188.4
70-80	-
80-85	156.7

Table 6-3. continued.

Core PS-III
Site 1 (Piscataqua River)
7-19-78

Depth (cm)	µg PAN[1]l
0-5	11.4
5-10	45.4
10-20	33.5
20-30	23.5
30-35	30.5

Bermuda Pore Water

Core FR-2[2]
Ferry Reach
June, 1978

Depth (cm)	µg PAN[1]l
4.5	153.1
7.0	73.0
9.0	90.0
11.0	81.0
13.5	71.2

Core CB-1[2]
Coot Bay
June, 1978

Depth (cm)	µg PAN[1]l
1.5	20.0
4.5	41.1
7.0	37.6
9.0	41.4
11.0	45.9
13.5	38.0

Core GS-1[2]
Great Sound
June, 1978

Depth (cm)	µg PAN[1]/l
4.5	12.6
7.5	10.8
10.5	18.1
13.0	23.8
15.5	13.1

1) PAN = primary amino nitrogen.

2) see Lyons et al. (1979c), for site descriptions.

comparison to the results from clastic sediments from Great Bay. The fluorescence method used for these determinations was described in detail in Chapter 2.

Concentrations of PAN in Great Bay pore waters were observed to range from about 214 µgN/l to 11 µgN/l, with the highest concentrations by far being observed at Site 4 (Footman Islands). The high concentrations of PAN at this site were not surprising, considering that eelgrass (Zostera marina), is a primary source of organic matter to the sediments at this site. As mentioned in Chapter 2, eelgrass has a relatively high protein content for a vascular plant. Overlying seawater concentrations are generally somewhat lower than this, ranging from about 15 µgN/l to less than 1 µgN/l (100 to 5 µg amino acids/l), (Clark et al., 1972; Lee and Bada, 1977; and Orem, 1980). This may suggest that bacterial removal relative to production of amino acids may be less in pore waters than in the overlying seawater (Gardner and Hanson, 1979). The pore water values for PAN from Great Bay sediments were similar to those observed by Gardner and Hanson (1979) in pore waters from a Georgia salt marsh (about 30 µgN/l), and Henrichs and Farrington (1979), in the Gulf of Maine and Buzzards Bay pore waters (from about 80 to 10 µgN/l). PAN concentrations in pore waters from Bermuda carbonate sediments (Table 6-3), were also similar to this, ranging from about 11 to 153 µgN/l. The highest PAN values in the Bermuda pore waters were observed at the Ferry Reach Site (FR-2).

Depth profiles of PAN in pore waters from gravity cores at Sites 1, 2 and 4 in Great Bay are illustrated in Figure 6-9. The rapid decrease in PAN concentration in the top 30 cm of the core from Site 4 is indicative of rapid microbial utilization of free amino acids in the

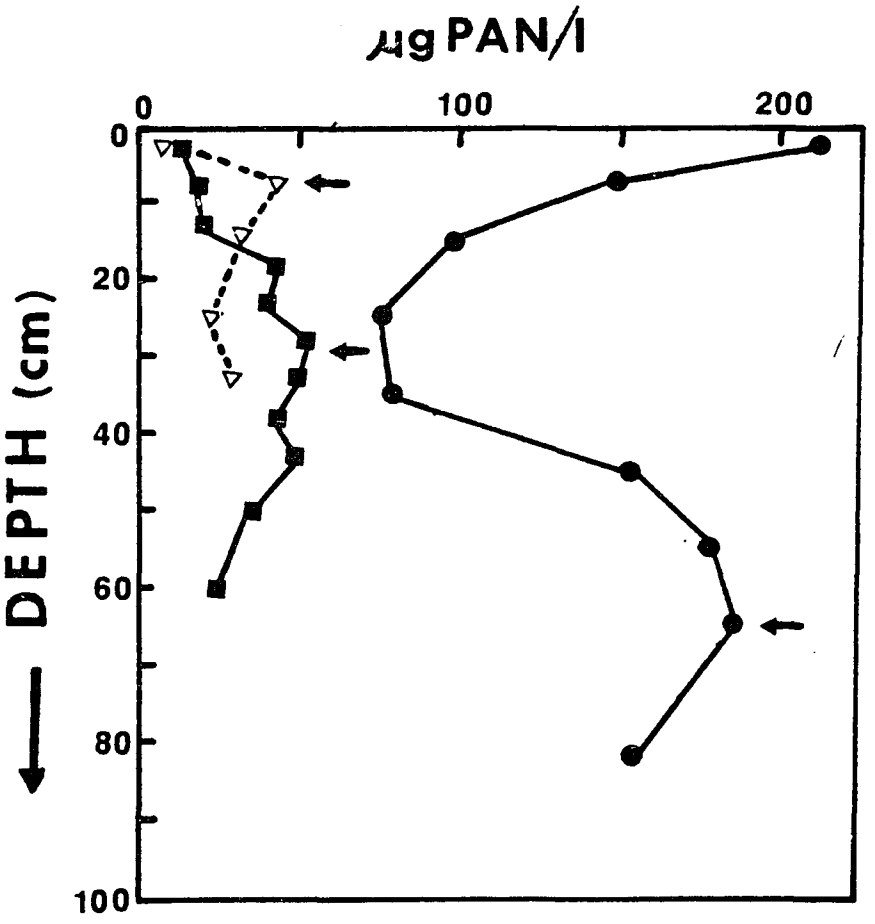

Figure 6-9. Concentrations of primary amino nitrogen (µgN/l), versus depth (cm), from Sites 1 (Δ--Δ), 2 (■—■), and 4 (●—●) in Great Bay. Arrows (⟵), indicate the interesting subsurface maxima observed in PAN concentration.

pore water. Recent work has indicated that free amino acids are readily utilized by sulphate reducing bacteria (Smith and Klug, 1981). Alternatively (or perhaps, in addition), condensation reactions involving the reaction of amino acids and sugars may be responsible for the observed profile in the upper 20 cm of this core. The lack of any similar trend at the two other sampling locations is probably related to their much lower concentrations.

It is interesting to note that all three of these cores showed subsurface maxima in PAN concentration (indicated by arrows in Figure 6-9), at various depths. As mentioned earlier, subsurface maxima have been observed for a number of specific organic compounds in anoxic marine pore waters, most notably for volatile fatty acids (Miller et al., 1979; and Barcelona, 1980). However, the significance of these subsurface maxima remains uncertain. Observed concentrations of biochemically active organic compounds represent the balance between production and consumption processes in the sediments. Thus, these concentration maxima are probably due to biochemical changes (e.g. changes in the nature of metabolic processes), occurring in the sediments as a function of depth. Since it is unlikely that the production of free amino acids from sedimentary proteins would increase at depths of 50 or 60 cm, these subsurface maxima probably mark a changeover in the types of labile organic compounds in the pore water that are metabolized. Indeed, at least in the core from Site 4, this subsurface maximum in PAN concentration may be indicative of a switchover from sulphate reduction to methanogenesis, as indicated by sulphate depletion (see Chapter 4).

Free Monosaccharides. Concentrations of dissolved free monosaccharides (presented as mg glucose equivalents/l), in pore waters

from gravity cores taken at Sites 1, 2 and 4 in Great Bay are presented in Table 6-4. In addition, pore water free monosaccharide concentrations from Bermuda carbonate sediments (the same cores as presented in the discussion on PAN, above), are also presented in this table for comparison. In Great Bay pore waters, free monosaccharide concentrations were observed to range from nearly 2 to less than 0.05 mg glucose/l. Pore waters from Bermuda carbonate sediments had a similar concentration range for free monosaccharides, with values from 3.4 to about 0.2 mg glucose/l. Lyons and co-workers (1979c), have observed dissolved carbohydrates (e.g. monosaccharides plus polysaccharides), to range from nearly 11 to less than 0.2 mg/l, in Bermuda pore waters. Using overall average values for dissolved monosaccharides and dissolved carbohydrates from Bermuda cores FR-2, CB-1 and GS-1 with data from this study and from Lyons et al. (1979c), it was determined that monosaccharides comprise about 64% of the total carbohydrates in Bermuda pore waters. No previous study of carbohydrates in pore waters from clastic marine sediments has appeared in the literature. This is surprising, considering the importance of carbohydrates in fermentation (Doelle, 1975). Obviously, more work is needed in this area, particularly an examination of the distribution of individual carbohydrates in marine pore waters.

Depth profiles of dissolved free monosaccharides (DFMS), in pore waters from the three Great Bay gravity cores are illustrated in Figure 6-10. No readily discernible trend with depth was observed in the cores from Sites 1 and 2. However, the core from Site 4 exhibited a depth profile very similar to that observed for PAN at this sampling location. In the top 30 cm of sediment, free monosaccharide concentra-

Table 6-4. Concentration of dissolved free monosaccharides (mg Glucose equivalents/l), in pore water from Great Bay clastic and Bermuda carbonate sediments.

Great Bay Pore Water

Core PS-I
Site 2 (Welsh Cove)
6-10-78

Depth (cm)	mg Glucose/l
0-5	0.21
5-10	0.79
10-15	1.23
15-20	-
20-25	0.53
25-30	1.58
30-35	0.90
35-40	1.40
40-45	1.03
45-55	0.53
55-65	1.50

Core PS-II
Site 4 (Footman Islands)
6-30-78

Depth (cm)	mg Glucose/l
0-5	1.47
5-10	0.61
10-20	<0.05
20-30	<0.05
30-40	0.08
40-50	0.20
50-60	0.22
60-70	0.45
70-80	-
80-85	-

Core PS-III
Site 1 (Piscataqua River)
7-19-78

Depth (cm)	mg Glucose/l
0-5	0.54
5-10	1.66
10-20	0.76
20-30	1.00

Table 6-4. continued.

Bermuda Pore Water

Core FR-2[1]
Ferry Reach
June, 1978

Depth (cm)	mg Glucose/l
4.5	2.08
7.0	3.42
9.0	1.25
11.0	1.18
13.5	0.80

Core CB-1[1]
Coot Bay
June, 1979

Depth (cm)	mg Glucose/l
1.5	0.21
4.5	-
7.0	0.29
9.0	0.37
11.0	0.61
13.5	2.31

Core GS-I[1]
Great Sound
June, 1978

Depth (cm)	mg Glucose/l
4.5	-
7.5	0.26
10.5	0.19
13.0	0.68

1) see Lyons et al. (1979c), for site description.

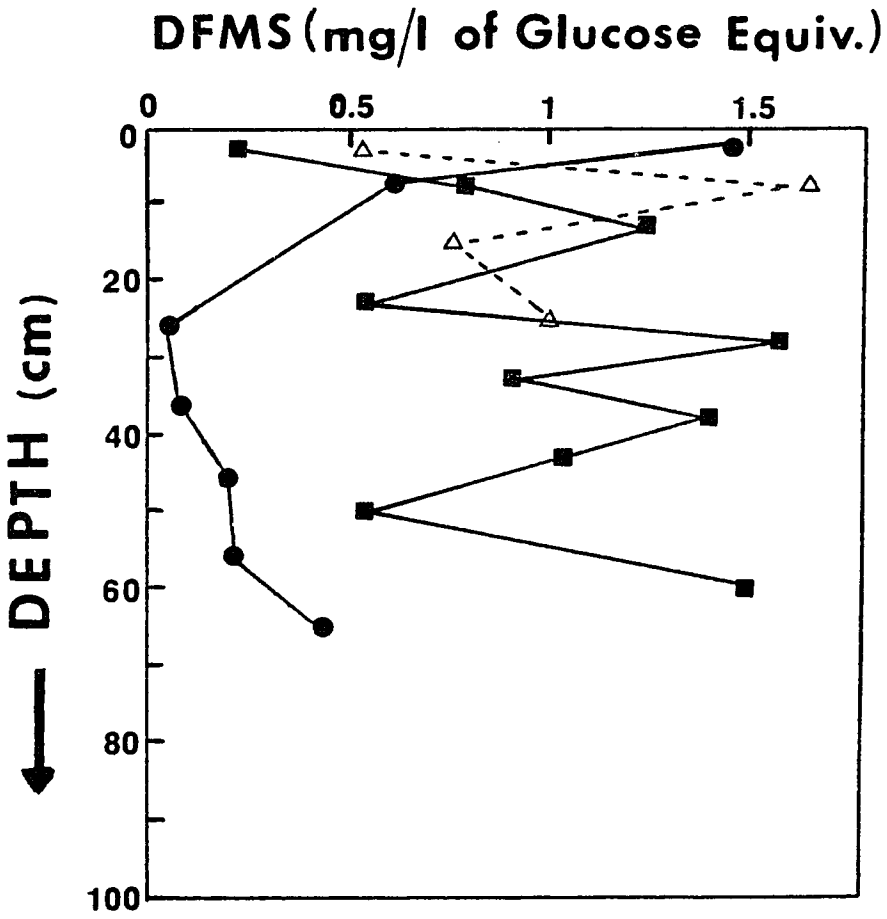

Figure 6-10. Concentrations of dissolved free monosaccharides (mg glucose equivalents/l), versus depth (cm), from Sites 1 (Δ- -Δ), 2 (■—■), and 4 (●—●), in Great Bay.

tions in the pore water were observed to decrease sharply with depth. As with PAN, this trend may reflect two simultaneously occurring processes: 1) rapid utilization of DFMS by sulphate reducing bacteria, and 2) the condensation of amino sugar polymers (e.g. melanoidins). Below 30 cm in this core, DFMS appeared to be approaching a subsurface maximum very similar to that observed for PAN. The possible biochemical significance of this subsurface maximum was discussed above. In the Bermuda cores, no consistent depth profile for DFMS at the different sites was observed. In core FR-2, a gradual decrease in pore water concentrations of DFMS was observed in the top 13.5 cm of sediment. This trend is consistent with what was observed for DFMS concentrations at Site 4 in Great Bay, and also with the results of Lyons and coworkers (1979c), for total dissolved carbohydrates in Bermuda pore waters. However, the CB-1 core showed a systematic increase in pore water concentrations of DFMS with depth. No systematic trend was observed for DFMS in the core from Site GS-1. These trends are difficult to rationalize with the limited data available here. However, depth trends of specific organic compounds in pore waters of carbonate sediments may be influenced by factors other than biochemical utilization and condensation reactions. Previous work has shown that carbonate sediments are active in adsorbing organic compounds (Suess, 1970 and 1973), and this process may have a profound influence on the observed pore water depth profiles of these species in this environment.

PAN and DFMS Percentages of DOC. Primary amino nitrogen and DFMS percentages of the total DOC in the pore waters from Sites 1, 2 and 4 in Great Bay are presented in Table 6-5. In the calculation of these percentages, amino acids were assumed to contain an average by

Table 6-5. Primary amino nitrogen and free monosaccharide percentages of dissolved organic carbon in Great Bay anoxic pore waters.

Core PS-I
Site 2 (Welsh Cove)
6-10-78

Depth (cm)	% PAN[1] of DOC	% DFMS[2] of DOC
0-5	0.106	0.21
5-10	0.272	0.15
10-15	0.283	2.31
15-20	0.553	-
20-25	0.503	0.89
25-30	0.585	2.34
30-35	0.494	1.2
35-40	0.407	1.74
40-45	0.365	1.03
45-55	0.282	0.58
55-65	0.202	1.63

Core PS-II
Site 4 (Footman Islands)
6-30-78

Depth (cm)	% PAN[1] of DOC	% DFMS[2] of DOC
0-5	1.29	1.20
5-10	0.912	0.50
10-20	0.441	<0.029
20-30	0.348	<0.031
30-40	0.362	0.048
40-50	0.458	0.079
50-60	0.545	0.090
60-70	0.519	0.168
70-80	-	-
80-85	0.424	-

Table 6-5. continued.

Core PS-III
Site 1 (Piscataqua River)
7-19-78

Depth (cm)	% PAN[1] of DOC	% DFMS[2] of DOC
0-5	0.0526	0.34
5-10	0.279	1.38
10-20	0.153	0.47
20-30	0.111	0.64
30-35	0.100	-

1) PAN = primary amino nitrogen

2) DFMS = dissolved free monosaccharides

weight of 14.30% N and 42.18% C (Supelco Inc., 1975), and glucose to contain 40.00% C (Supelco Inc., 1975). In general, both amino acids and monosaccharides constitute less than 1% of the DOC in Great Bay pore waters. Amino acids ranged from 1.3% to 0.05% of the DOC, while monosaccharides comprised from 2.3% to less than 0.03% of the organic carbon in the pore water. Average values for PAN and DFMS percentages, respectively, were: 0.1% and 0.7% at Site 1, 0.4% and 1.2% at Site 2, and 0.6% and 0.3% at Site 4. Overall, PAN constituted an average of 0.4% and DFMS an average of 0.8% of the DOC in Great Bay pore waters. The very low percentages of these compounds in relation to the total amount of organic matter present in anoxic marine pore waters is not surprising, considering the reactivity (both biological and chemical), of these substances. A large percentage of the DOC in anoxic marine pore waters may consist of large polymeric substances similar to humic substances or melanoidin (Nissenbaum et al., 1972). Indeed, the ultrafiltration results of pore water DOC presented in Chapter 5 strongly suggests this. Lyons and co-workers (1979c), observed dissolved carbohydrates to constitute a significant percentage of the dissolved organic matter in a few surface samples from Bermuda carbonate sediments (e.g. up to 70%). However, this percentage was observed to decrease sharply with depth to values more in agreement with the results from this study (e.g. 2% to 5% of the dissolved organic matter).

III. Conclusions

The results presented in this chapter generally support the concept of the increased condensation of organic matter in estuarine pore waters with depth in the sediments, as first suggested by Nissenbaum and co-workers (1972), and Krom and Sholkovitz (1977). Fractiona-

tion of the pore water organic matter from Great Bay sediments using HPLC has shown the gradual decrease in the polarity of this material with depth. Spectroscopic studies of this material by ultraviolet/visible absorption and fluorometry yielded results generally similar to those observed by previous workers (Nissenbaum et al., 1972; Krom and Sholkovitz, 1977; and Ewald, 1979). Little structure was observed in any of these spectra, even following fractionation of the pore water organic matter by HPLC. Both the ultraviolet/visible absorption and fluorescence spectra of pore water organic matter were similar to those of sedimentary marine humic and fulvic acids, reinforcing the model proposed by Krom and Sholkovitz (1977), for the formation of these substances by the condensation of low molecular weight organic compounds in pore water.

Studies of primary amino nitrogen and free monosaccharides in estuarine pore waters from Great Bay clastic and Bermuda carbonate sediments have shown these compounds to constitute only a small fraction of the DOC, usually less than 1%. However, this may be indicative of rapid utilization of these compounds by sedimentary microorganisms or the rapid condensation of these chemical species in anoxic pore waters, rather than a lack of any significance. In many of these cores, curious subsurface concentration maxima for primary amino nitrogen and free monosaccharides were observed, which may be indicative of a transition in the bacterial metabolic zones in the sediments (i.e. from sulphate reduction to methanogenesis).

CHAPTER 7

OVERALL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

I. Overall Conclusions

The research presented in this dissertation was carried out in order to obtain information on the organic geochemistry of estuarine sediments. The importance of understanding in detail the transformations affecting organic molecules deposited in estuarine sediments was elaborated in Chapter 1. Aside from the importance of these transformations in the genesis of fossil fuels, the process of organic decay in marine sediments probably plays a key role in the cycling of many elements on earth. Unfortunately, much remains to be accomplished in this field. It is hoped that the results of this work have provided some advances in our understanding of this system.

The approach taken in this study was somewhat unusual in that the analysis of pore water organic matter was emphasized over that of sedimentary organic matter. As noted in previous discussions, few workers have used this approach, despite its advantages (see Chapter 1). As a result, little baseline data on the organic geochemistry of marine pore waters exists, and in many ways this dissertation has provided more 'jumping-off' points for future work than anything else.

Specific conclusions regarding the results of individual projects have been discussed at the end of each chapter. However, a number of the more important conclusions from this study are presented below:

1) The necessity of excluding atmospheric oxygen during sampling, processing and analysis of anoxic pore waters was demonstrated. The exposure of anoxic pore waters to oxygen resulted in changes in both the amounts and nature of the dissolved organic matter, as well as quantitative changes in a number of dissolved inorganic species.

2) Lateral, vertical and seasonal changes in pore water organic matter from Great Bay sediments were observed. The gradual increases in DOC with depth in the sediments was attributed to the gradual accumulation of bacterial metabolic products in the pore water, and the slowness of diffusion. The seasonal variation of DOC in surficial sediments was shown to be coupled to seasonal changes in microbial activities and the bioturbation of marine benthic organisms. In deeper sediments, the seasonal changes in DOC were explained in terms of an adsorption/ desorption mechanism, probably temperature induced. This process may be coupled to similar large seasonal changes in the concentrations of dissolved ammonia and phosphate in deep sediments.

3) The molecular size of pore water organic matter was observed to be relatively large, with the dominant molecular weight range in many cores being between 50,000 and 1,000. In most cores, the overall molecular weight of this material was observed to increase with depth in the sediments, indicating that condensation reactions and the formation of organic geopolymers (e.g. humic and fulvic acids), may be occurring in these pore waters. This idea is also supported by the similarity of ultraviolet/visible absorption and fluorescence spectra of pore water organic matter to those of humic and fulvic acids.

4) A method for the separation of pore water organic matter into fractions was developed using reversed phase HPLC, and the usefulness of this technique for qualitative studies of pore water organic matter was demonstrated. The relative polarity of pore water organic matter was observed to decrease with depth (in accordance with the condensation reaction theory), using this technique.

5) From measured depth profiles of sulphate, ammonia and phosphate, rates of sulphate reduction and ammonia and phosphate production were calculated using a kinetic model (Berner, 1980). Calculated

values of sulphate reduction at two sites in Great Bay agreed quite well with measured rates (Hines, 1981).

6) Depth profiles of primary amino nitrogen and free monosaccharides in pore water from a number of cores in Great Bay exhibited subsurface concentration maxima. These maxima were considered indicative of the changeover from one anaerobic metabolic process in the sediments to another (e.g. from sulphate reduction to methanogenesis).

II. Suggestions For Future Work

As mentioned in Chapter 1, organic geochemical studies should incorporate both the bulk organic and specific organic compounds approach in the solution of problems, in order to achieve maximal success. This dual approach has been used here in studies of the organic geochemistry of anoxic pore waters from Great Bay, New Hampshire, and although some progress has been made in understanding this system, a great deal remains to be achieved.

The work presented in Chapter 3 has demonstrated quite clearly that exposure of anoxic marine pore waters to atmospheric oxygen results in both qualitative and quantitative changes in the dissolved organic matter. Thus, it is essential that future organic geochemical studies of anoxic sediments use strict anoxic conditions during sample collection, processing, storage and analysis in order to maintain sample integrity. Aside from this important point, this study implies that much of the dissolved organic matter in anoxic pore water is relatively unstable, possibly existing as oxygen sensitive conjugated systems (aromatic and/or olifinic). Future studies should emphasize an analysis of the nature of these oxidative changes. High resulution NMR might prove particularly useful in such work.

The use of HPLC as a tool for the fractionation and character-

ization of pore water organic matter in this study, represented only preliminary work and a hint at the potential of this technique. Certainly, the solvent system developed for this work does not necessarily represent the ultimate in separation efficiency for pore water organic matter, but more of a starting point. A vast array of other mobile phase combinations used isocratically and with gradient elution remain to be tried in future work. In addition, other stationary phases might also be tried in future studies.

The off-line coupling of HPLC to spectroscopic methods of analysis (Chapter 6), in attempts to define some of the structural characteristics of pore water organic matter in this study were relatively unsuccessful. Ultraviolet/visible absorption and fluorescence spectroscopy of the various HPLC fractions provided little structural information, and insufficient sample was obtained from the HPLC effluent of the various fractions for infrared absorption or NMR spectroscopic results to be secured. However, future work in the off-line coupling of HPLC to infrared absorption and NMR spectroscopy might be able to achieve sufficient sample for spectroscopic analysis in two ways: 1) preconcentration of the pore water organic matter using ultrafiltration prior to injection onto a semi-preparatory reversed phase column, and 2) the use of preparatory scale HPLC, allowing the injection of large volumes of pore water directly onto the column. The off-line coupling of HPLC, particularly with high resolution NMR in this manner, might provide valuable structural information on the nature of pore water organic matter.

The studies presented in Chapter 4 and 5 on the lateral, vertical and seasonal variations of inorganic species and DOC and the molecular

weight distributions of DOC and iron in Great Bay pore waters were fairly complete. However, there are still a number of questions that should be pursued in future work. For example, the temperature induced solubility effect, used to explain large seasonal variations in dissolved ammonia, phosphate and DOC in deep sections of gravity cores needs to be confirmed. This could be accomplished by attempts to artificially induce this effect on natural sediment samples in the laboratory. Another project that should be undertaken is an investigation of the nature of the predominantly high molecular weight iron observed in anoxic pore waters. In particular, the question of whether this iron is associated with large organic polymers or inorganic colloids should be addressed. In addition, similar studies in other estuaries for comparison to the results obtained in this work for Great Bay would be of value.

Finally, a great deal of further work in the analysis of specific compounds in anoxic pore water needs to be accomplished before any real understanding of the biogeochemistry of this system can be achieved. To date, the only group of compounds that have been investigated in any detail in this system have been the amino acids (e.g. Henrichs and Farrington, 1979; and Gardner and Hanson, 1979). In particular, studies of carbohydrates and fatty acids in anoxic pore waters are needed, since these compounds may be extremely important in anaerobic bacterial metabolism (Doelle, 1975). Such studies should be undertaken jointly with microbiological work in order to achieve maximum information on microbial/organic matter interactions in anoxic marine sediments.

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APPENDICES

APPENDIX A

SOLID SEDIMENT RESULTS

I. Sediment Size

A. Site 1 (Piscataqua River)

Core PS-III
Date: 7-19-78

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)
0-5	56.91	27.55	15.52	43.09
5-10	67.06	20.53	12.41	32.94
10-20	70.59	19.41	10.00	29.41
20-30	74.24	16.30	9.458	25.76
30-35	78.36	14.76	6.880	21.64
35-40	89.95	6.979	3.075	10.05

B. Site 2 (Welsh Cove)

Core PS-I
Date: 6-10-78

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)
0-5	78.32	12.88	8.814	21.69
5-10	68.40	22.29	9.306	31.60
10-15	58.42	27.46	16.56	44.02
15-20	-	-	-	-
20-25	31.36	46.36	22.28	68.64
25-30	27.21	47.93	32.31	80.24
30-35	32.31	44.85	22.84	67.69
35-40	29.51	44.70	25.81	70.51
40-45	36.52	40.55	22.92	63.47
45-55	43.71	37.10	19.19	56.29
55-65	19.18	51.76	20.96	80.82

C. Site 3 (Adams Cove)

Core UF-IV
Date: 7-11-80

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)
0-15	49.28	41.68	9.042	50.72
15-30	48.57	49.53	1.904	51.43
30-45	54.06	44.59	1.353	45.94
45-60	54.27	41.89	3.842	45.73
60-75	34.97	63.74	1.292	65.03
75-90	42.48	46.38	11.14	57.52

D. Site 4 (Footman Islands)

Core PS-II
Date: 6-30-78

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)
0-5	45.89	30.63	23.47	54.10
5-10	19.20	47.10	33.70	80.80
10-20	31.76	35.85	32.39	68.24
20-30	17.93	41.67	40.40	82.07
30-40	18.53	41.24	40.23	81.47
40-50	25.88	38.94	35.18	74.12
50-60	21.16	51.77	27.07	78.84
60-70	47.34	29.08	23.58	52.66
70-80	75.73	14.66	9.608	24.27
80-85	89.48	5.152	5.370	10.52

Core UF-VII
Date: 8-11-80

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)
0-15	37.65	50.67	11.68	62.35
15-30	30.19	67.06	2.747	69.81
30-45	37.85	47.71	14.44	62.15
45-60	27.85	54.30	17.85	72.15
60-75	41.95	47.26	10.79	58.05

E. Site 5 (Squamscott River)

Core PS-IV
Date: 8-10-78

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)
0-10	53.53	38.15	8.321	46.47
10-20	33.78	42.25	20.97	66.22
20-30	20.57	47.42	32.01	79.43
30-40	29.36	42.90	27.74	70.64
40-50	32.28	40.52	27.20	67.72
50-60	37.62	39.80	22.58	62.38
60-70	34.25	37.38	28.37	65.75
70-80	30.29	41.23	28.48	69.71
80-90	39.12	34.68	26.20	60.88
90-100	35.95	36.10	27.95	64.05

II. Organic Carbon, Nitrogen and Phosphorus and Inorganic Phosphorus

A. Site 1 (Piscataqua River)

Core PS-III
Date: 7-19-78

Depth (cm)	Organic C (%)	Organic N (%)	Organic P (%)	Inorganic P (%)
0-5	1.51	0.17	0.0048	0.0211
5-10	1.00	0.09	0.0072	0.0184
10-20	1.92	0.15	0.0192	0.0055
20-30	0.97	0.10	0.0096	0.0141
30-35	0.79	0.10	-	-
35-40	0.76	0.05	0.0001	0.0149

B. Site 2 (Welsh Cove)

Core PS-I
Date: 6-10-78

Depth (cm)	Organic C (%)	Organic N (%)	Organic P (%)	Inorganic P (%)
0-5	0.80	0.10	0.0052	0.0201
5-10	0.73	0.09	0.0048	0.0201
10-15	1.00	0.11	0.0130	0.0188
15-20	1.48	0.17	0.0056	0.0260
20-25	1.14	0.18	0.0020	0.0231
25-30	1.45	0.16	0.0099	0.0217
30-35	1.16	0.13	-	-
35-40	1.42	0.17	0.0118	0.0196
40-45	1.35	0.14	0.0091	0.0217
45-55	1.24	0.13	0.0073	0.0218
55-65	1.60	0.15	0.0112	0.0229

C. Site 3 (Adams Cove)

Core UF-IV
Date: 7-11-80

Depth (cm)	Organic C (%)	Organic N (%)	Organic P (%)	Inorganic P (%)
0-15	1.93	0.17	0.0090	0.0485
15-30	1.83	0.18	0.0039	0.0473
30-45	0.99	0.11	0.0058	0.0408
45-60	0.96	0.10	0.0001	0.0486
60-75	1.01	0.09	-	-
75-90	1.03	0.10	0.0001	0.0470

D. Site 4 (Footman Islands)

Core PS-II
Date: 6-30-78

Depth (cm)	Organic C (%)	Organic N (%)	Organic P (%)	Inorganic P (%)
0-5	2.21	0.22	0.0037	0.0232
5-10	2.98	0.49	0.0098	0.0244
10-20	2.61	0.34	0.0095	0.0239
20-30	2.76	0.36	0.0134	0.0238
30-40	2.97	0.32	-	-
40-50	3.46	0.85	0.0147	0.0213
50-60	1.79	0.40	0.0011	0.0256
60-70	1.23	0.20	0.0133	0.0159
70-80	1.89	0.21	0.0072	0.0170
80-85	0.65	0.07	-	-

Core UF-VII
Date: 8-11-80

Depth (cm)	Organic C (%)	Organic N (%)	Organic P (%)	Inorganic P (%)
0-15	2.20	0.21	0.0072	0.0489
15-30	2.97	0.31	0.0124	0.0450
30-45	3.57	0.33	0.0068	0.0532
45-60	3.87	0.37	0.0144	0.0525
60-75	3.41	0.36	0.0078	0.0574

E. Site 5 (Squamscott River)

Core PS-IV
Date: 8-10-78

Depth (cm)	Organic C (%)	Organic N (%)	Organic P (%)	Inorganic P (%)
0-10	2.44	0.29	0.0125	0.0196
10-20	2.26	0.29	0.0095	0.0141
20-30	2.71	0.31	0.0143	0.0143
30-40	2.34	0.27	0.0127	0.0132
40-50	2.82	0.29	0.0224	0.0144
50-60	2.99	0.28	0.0062	0.0193
60-70	3.77	0.32	0.0202	0.0126
70-80	3.56	0.29	0.0133	0.0152
80-90	3.24	0.25	0.0139	0.0170
90-100	4.05	0.33	0.0161	0.0172

III. Molar Ratios of Sedimentary Organic and Inorganic Matter

A. Site 1 (Piscataqua River)

Core PS-III
Date: 7-19-78

Depth (cm)	OC/ON	OC/OP	ON/OP	IP/OP
0-5	10.4	815	78.8	4.39
5-10	13.0	357	27.5	2.53
10-20	14.8	258	17.4	0.287
20-30	11.3	262	23.3	1.47
30-35	9.16	-	-	-
35-40	16.9	3310	195	25.3

B. Site 2 (Welsh Cove)

Core PS-I
Date: 6-10-78

Depth (cm)	OC/ON	OC/OP	ON/OP	IP/OP
0-5	9.55	398	41.7	3.86
5-10	9.51	387	40.7	4.16
10-15	10.1	199	19.8	1.45
15-20	10.4	675	65.1	4.61
20-25	7.35	1480	202	11.7
25-30	10.6	379	35.7	2.19
30-35	10.5	-	-	-
35-40	9.83	310	31.6	1.66
40-45	11.1	379	34.1	2.38
45-55	10.9	439	40.4	2.99
55-65	12.2	369	30.3	2.04

C. Site 3 (Adams Cove)

Core UF-IV
Date: 7-11-80

Depth (cm)	OC/ON	OC/OP	ON/OP	IP/OP
0-15	13.2	553	41.8	5.39
15-30	11.9	1210	102	12.1
30-45	10.5	440	41.9	7.03
45-60	11.2	-	-	-
60-75	13.1	-	-	-
75-90	12.0	-	-	-

D. Site 4 (Footman Islands)

Core PS-II
Date: 6-30-78

Depth (cm)	OC/ON	OC/OP	ON/OP	IP/OP
0-5	11.8	1560	133	6.34
5-10	7.12	784	110	2.49
10-20	9.06	710	78.4	2.52
20-30	8.84	530	60.0	1.77
30-40	10.6	-	-	-
40-50	4.75	609	128	1.46
50-60	5.21	4020	772	22.3
60-70	7.05	237	33.6	1.19
70-80	10.6	677	63.7	2.37
80-85	11.2	-	-	-

Core UF-VII
Date: 8-11-80

Depth (cm)	OC/ON	OC/OP	ON/OP	IP/OP
0-15	12.2	788	64.5	6.79
15-30	11.2	618	55.3	3.63
30-45	12.6	1350	107	7.82
45-60	12.2	693	56.8	3.65
60-75	11.0	1130	102	7.36

E. Site 5 (Squamscott River)

Core PS-IV
Date: 8-10-78

Depth (cm)	OC/ON	OC/OP	ON/OP	IP/OP
0-10	9.93	506	51.0	1.57
10-20	9.07	614	67.7	1.48
20-30	10.3	490	45.9	1.00
30-40	9.99	477	47.7	1.04
40-50	11.5	324	28.2	0.644
50-60	12.4	1240	99.8	3.10
60-70	13.8	482	35.0	0.624
70-80	14.2	691	48.6	1.15
80-90	14.9	601	40.5	1.22
90-100	14.3	650	45.5	1.07

APPENDIX B

PORE WATER INORGANIC SPECIES: BOX CORES

I. pH

A. Site 3 (Adams Cove)

Depth (cm)	pH			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	7.20	6.99	7.52	7.41
2-4	7.35	6.88	7.45	7.53
4-6	7.48	7.34	7.42	7.53
6-8	7.52	7.43	7.42	7.52
8-10	7.63	7.52	7.50	7.53
10-12	7.73	7.55	7.35	7.58

Depth (cm)	pH			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	7.31	7.53	7.40	7.40
2-4	7.24	7.45	7.47	7.14
4-6	7.28	7.43	7.37	7.45
6-8	7.28	7.39	7.38	7.50
8-10	7.32	7.39	7.39	7.22
10-12	7.43	7.43	7.42	7.54

B. Site 4 (Footman Islands)

Depth (cm)	pH			
	4-26-79	6-10-79	7-23-79	9-12-79
0-2	7.31	7.13	7.18	7.11
2-4	7.16	7.16	7.22	7.19
4-6	7.16	7.14	7.19	7.27
6-8	7.27	7.12	7.17	7.28
8-10	7.02	7.17	7.24	7.07
10-12	7.17	7.14	7.20	7.10

II. Titration Alkalinity

A. Site 3 (Adams Cove)

Depth (cm)	Titration Alkalinity (meq/l)			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	2.87	2.68	2.45	4.49
2-4	3.34	3.59	2.93	6.42
4-6	4.13	4.84	3.31	9.75
6-8	4.79	6.30	4.19	10.41
8-10	4.92	8.03	-	12.10
10-12	5.09	7.11	4.80	12.51

Depth (cm)	Titration Alkalinity (meq/l)			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	2.67	3.60	3.20	3.36
2-4	4.17	4.42	5.73	3.68
4-6	6.89	4.64	5.89	4.05
6-8	12.62	5.42	2.35	4.15
8-10	13.91	5.93	7.96	5.11
10-12	15.94	6.44	9.37	5.59

B. Site 4 (Footman Islands)

Depth (cm)	Titration Alkalinity (meq/l)			
	4-26-79	6-10-79	7-23-79	9-12-79
0-2	2.14	2.28	3.35	2.56
2-4	2.18	2.59	3.11	3.97
4-6	2.51	2.89	3.47	5.49
6-8	2.85	2.89	4.64	5.81
8-10	3.36	2.77	4.29	5.56
10-12	3.32	3.00	3.31	5.81

III. Chlorinity

A. Site 3 (Adams Cove)

Depth (cm)	Chlorinity (°/oo)			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	14.4	10.4	9.4	11.5
2-4	12.6	10.1	9.7	10.7
4-6	10.2	9.8	9.6	10.1
6-8	8.1	9.7	9.5	9.9
8-10	6.4	8.6	9.4	9.5
10-12	4.9	8.8	8.6	9.1

Depth (cm)	Chlorinity (°/oo)			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	13.5	15.3	15.9	15.5
2-4	13.1	15.4	15.4	15.1
4-6	12.0	14.9	14.9	15.2
6-8	11.2	14.4	13.9	13.9
8-10	10.8	13.6	12.1	-
10-12	10.8	12.5	10.7	12.1

B. Site 4 (Footman Islands)

Depth (cm)	Chlorinity (°/oo)			
	4-26-79	6-10-79	7-23-79	9-12-79
0-2	10.7	9.7	14.8	14.9
2-4	9.4	9.6	15.0	14.6
4-6	8.9	9.2	13.6	14.9
6-8	8.8	8.9	13.8	14.2
8-10	9.5	8.8	13.2	14.1
10-12	10.0	9.7	13.3	13.9

IV. Ammonia

A. Site 3 (Adams Cove)

Depth (cm)	Ammonia (μM)			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	69.9	148	116	280
2-4	135	216	144	364
4-6	196	264	169	436
6-8	240	352	215	619
8-10	264	464	-	688
10-12	231	379	215	735

Depth (cm)	Ammonia (μM)			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	157	193	213	93.6
2-4	271	275	353	95.5
4-6	549	311	484	146
6-8	671	369	496	193
8-10	823	383	524	230
10-12	890	449	553	241

V. Phosphate

A. Site 3 (Adams Cove)

Depth (cm)	Phosphate (μM)			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	2.4	4.3	23.8	78.6
2-4	10.7	95.8	36.7	135
4-6	60.0	77.8	46.7	142
6-8	91.5	84.7	53.7	163
8-10	113	87.6	-	159
10-12	79.5	95.8	125	152

Depth (cm)	Phosphate (μM)			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	69.0	3.4	34.1	19.4
2-4	86.8	14.5	78.1	21.0
4-6	179	23.1	32.1	31.3
6-8	237	104	109	40.0
8-10	285	107	109	62.9
10-12	308	123	113	58.0

VI. Total Iron

A. Site 3 (Adams Cove)

Depth (cm)	Total Iron (ppm)			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	1.28	10.1	9.75	8.43
2-4	0.93	4.90	2.23	2.17
4-6	0.33	1.41	1.39	1.30
6-8	0.36	0.30	1.30	0.37
8-10	0.28	-	-	0.24
10-12	-	0.31	0.71	0.38

Depth (cm)	Total Iron (ppm)			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	23.7	11.5	15.7	5.45
2-4	-	4.92	7.88	3.90
4-6	13.8	5.58	-	4.86
6-8	9.62	2.56	3.39	2.68
8-10	6.40	3.89	1.32	-
10-12	1.13	1.85	0.63	1.65

VII. Sulphate

A. Site 3 (Adams Cove)

Depth (cm)	Sulphate (mM)			
	3-10-80	4-9-80	5-2-80	5-20-80
0-2	14.6	13.1	11.6	11.7
2-4	12.8	12.4	12.2	11.3
4-6	10.0	12.3	11.8	10.7
6-8	8.2	11.5	10.8	6.90
8-10	4.7	9.1	7.7	4.36
10-12	2.1	5.8	-	3.96

Depth (cm)	Sulphate (mM)			
	6-2-80	7-2-80	8-1-80	11-14-80
0-2	10.5	19.7	21.1	39.1
2-4	9.61	19.5	20.1	29.8
4-6	12.7	17.7	18.7	30.2
6-8	10.1	16.9	16.1	28.7
8-10	8.59	15.2	13.1	26.7
10-12	6.73	13.4	9.23	24.9

APPENDIX C

PORE WATER INORGANIC SPECIES: GRAVITY CORES

I. pH, Titration Alkalinity and Chlorinity

A. Site 1 (Piscataqua River)

Core UV-VI
Date: 8-11-80

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-10	7.38	3.58	15.6
10-20	7.63	12.88	15.6
20-30	7.48	18.52	15.6
30-40	7.72	-	-
40-50	7.74	-	-
50-60	7.96	-	-

B. Site 2 (Welsh Cove)

NO DATA

C. Site 3 (Adams Cove)

Core UF-IV
Date: 7-11-80

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-15	7.28	6.66	14.3
15-30	7.22	6.86	10.4
30-45	7.27	0.59	7.5
45-60	7.40	5.52	4.4
60-75	7.17	1.03	3.6
75-90	7.11	1.94	3.4

D. Site 4 (Footman Islands)

Core OAX-I
Date: 6-23-80

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-15	7.33	3.88	13.4
15-30	7.47	8.57	13.7
30-45	7.35	15.28	13.7
45-60	7.64	22.71	13.8
60-75	7.60	26.90	13.7
75-90	7.50	27.42	13.4

Core UF-VII
Date: 8-11-80

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-15	7.22	13.55	13.6
15-30	7.20	42.63	13.3
30-45	7.18	60.65	13.4
45-60	7.15	65.99	13.3
60-75	7.14	68.69	13.3

Core OAX-II
Date: 10-21-80

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-15	6.95	4.01	16.4
15-30	7.45	9.08	14.5
30-45	7.79	16.52	14.2
45-60	7.87	25.16	14.5
60-75	7.57	27.23	14.3
75-90	7.30	30.69	14.4

Core UF-IX
Date: 4-15-81

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-15	7.00	5.32	13.3
15-30	7.43	10.04	14.6
30-45	7.13	15.73	14.8
45-60	7.40	18.01	14.5
60-65	7.87	21.14	-

E. Site 5 (Squamscott River)

Core UF-V
Date: 7-11-80

Depth (cm)	pH	Titration Alkalinity (meq/l)	Chlorinity (°/oo)
0-15	7.20	2.34	14.1
15-30	7.05	16.12	12.3
30-45	7.09	24.89	12.5
45-60	7.08	24.27	12.1
60-75	7.12	33.64	11.9

II. Ammonia, Phosphate, Total Iron and Sulphate

A. Site 1 (Piscataqua River)

Core PS-III
Date: 7-19-78

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-5	622	56.4	-	-
5-10	1200	104	-	-
10-20	-	-	-	-
20-30	584	517	-	-
30-35	-	-	-	-
35-40	-	-	-	-

Core UF-VI
Date: 8-11-80

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-10	223	51.2	2.12	24.5
10-20	796	166	3.39	18.2
20-30	1060	185	3.29	-

B. Site 2 (Welsh Cove)

Core PS-I
Date: 6-10-78

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-5	-	-	-	-
5-10	282	54.2	-	-
10-15	-	-	-	-
15-20	613	36.8	-	-
20-25	742	42.7	-	-
25-30	911	56.1	-	-
30-35	1090	68.2	-	-
35-40	1180	75.4	-	-
40-45	1190	72.1	-	-
45-50	1670	94.8	-	-
50-55	1910	105	-	-

C. Site 3 (Adams Cove)

Core UF-IV
Date: 7-11-80

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-15	377	78.1	0.15	18.0
15-30	497	57.5	0.15	10.6
30-45	647	63.2	-	4.65
45-60	459	21.1	0.24	2.07
60-75	511	29.7	0.56	0.71
75-90	1120	25.1	0.32	0.01

D. Site 4 (Footman Islands)

Core PS-II
Date: 6-30-78

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-5	1550	88.7	-	-
5-10	3680	346	-	-
10-20	6440	455	-	-
20-30	8210	1120	-	-
30-40	10800	656	-	-
40-50	-	-	-	-
50-60	11900	603	-	-
60-70	13100	471	-	-
70-80	-	-	-	-
80-85	-	-	-	-

Core OAX-I
Date: 6-23-80

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-15	44.7	28.8	0.24	18.5
15-30	263	86.5	-	14.4
30-45	561	132	0.15	12.6
45-60	528	105	0.28	5.98
60-75	548	110	0.17	0.30
75-90	701	112	0.12	0.19

Core UF-VII
Date: 8-11-80

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-15	715	123	1.68	13.8
15-30	2650	271	0.92	2.26
30-45	4240	340	1.12	0.64
45-60	5230	471	3.82	0.05
60-75	5610	457	3.09	0.01

Core OAX-II
Date: 10-21-80

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-15	129	22.5	0.91	22.6
15-30	384	87.6	3.82	14.5
30-45	1090	113	1.43	8.27
45-60	1600	120	1.14	5.41
60-75	1960	112	4.49	4.19
75-90	2590	118	-	1.86

Core UF-IX
Date: 4-15-81

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-15	715	98.3	6.81	22.5
15-30	2170	173	4.50	4.51
30-45	2650	146	1.13	0.10
45-60	2880	112	6.94	0.01
60-75	-	-	6.18	0.01

E. Site 5 (Squamscott River)

Core PS-IV
Date: 8-10-78

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-10	1090	69.1	-	-
10-20	5110	481	-	-
20-30	-	-	-	-
30-40	6670	532	-	-
40-50	8850	605	-	-
50-60	10000	651	-	-
60-70	10800	693	-	-
70-80	11000	739	-	-
80-90	12500	734	-	-
90-100	12900	775	-	-

Core UF-V
Date: 7-11-80

Depth (cm)	Ammonia (μM)	Phosphate (μM)	Total Iron (ppm)	Sulphate (mM)
0-15	357	69.6	0.35	35.6
15-30	1090	135	0.15	25.8
30-45	1740	203	0.17	5.97
45-60	2550	574	0.19	2.39
60-75	2960	292	0.21	0.01

APPENDIX D

DISSOLVED ORGANIC CARBON ULTRAFILTRATION RESULTS

I. Core UF-I

Date: 4-6-79
Site 4 (Footman Islands)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-10	Total	59.7	-
	>50,000	43.6	73
	<50,000	16.1	27
10-20	Total	70.1	-
	>50,000	13.0	19
	<50,000	57.1	81
50-60	Total	51.4	-
	>50,000	4.0	8
	<50,000	47.4	92
60-70	Total	56.4	-
	>50,000	3.4	6
	<50,000	53.0	94
70-80	Total	54.3	-
	>50,000	3.4	6
	<50,000	50.9	94
80-90	Total	45.6	-
	>50,000	4.3	9
	<50,000	41.3	91

II. Core UF-II

Date: 6-20-79
Site 4 (Footman Islands)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-10	Total	166.3	-
	>10,000	137.9	83
	<10,000	28.4	17
10-20	Total	52.6	-
	>10,000	24.8	47
	<10,000	27.8	53
30-40	Total	98.6	-
	>10,000	42.8	43
	<10,000	55.8	57
50-60	Total	127.6	-
	>10,000	29.0	23
	<10,000	98.6	77
60-70	Total	74.4	-
	>10,000	15.7	21
	<10,000	58.7	79

III. Core OAX-I

Date: 6-23-80
Site 4 (Footman Islands)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-15	Total	14.3	-
	>50,000	6.2	43
	50,000-1,000	3.4	24
	<1,000	4.7	33
15-30	Total	29.1	-
	>50,000	11.0	38
	50,000-1,000	13.7	47
	<1,000	4.4	15
30-45	Total	46.5	-
	>50,000	8.0	17
	50,000-1,000	33.3	72
	<1,000	5.2	11
45-60	Total	46.7	-
	>50,000	10.7	23
	50,000-1,000	28.9	62
	<1,000	7.1	15
60-75	Total	46.1	-
	>50,000	10.1	22
	50,000-1,000	31.0	67
	<1,000	5.0	11
75-90	Total	50.1	-
	>50,000	11.8	24
	50,000-1,000	34.7	69
	<1,000		

IV. Core UF-IV

Date: 7-11-80
Site 3 (Adams Cove)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-15	Total	8.3	-
	>50,000	1.0	12
	50,000-10,000	-	-
	10,000-1,000	-	-
	<1,000		
15-30	Total	10.2	-
	>50,000	1.8	18
	50,000-10,000	1.6	16
	10,000-1,000	5.1	50
	<1,000	1.7	16
30-45	Total	18.7	-
	>50,000	7.4	39
	50,000-10,000	-	-
	10,000-1,000	-	-
	<1,000	-	-
45-60	Total	14.8	-
	>50,000	7.5	51
	50,000-10,000	0.9	6
	10,000-1,000	2.6	18
	<1,000	3.8	25
60-75	Total	200.2	-
	>50,000	47.4	24
	50,000-10,000	85.7	43
	10,000-1,000	60.0	30
	<1,000	7.0	3
75-90	Total	19.8	-
	>50,000	0.4	2
	50,000-10,000	-	-
	10,000-1,000	-	-
	<1,000	3.4	17

V. Core UF-V

Date 7-11-80
Site 5 (Squamscott River)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-15	Total	7.6	-
	>50,000	1.2	16
	50,000-10,000	0.4	5
	10,000-1,000	0.2	3
	<1,000	5.8	76
15-30	Total	24.6	-
	>50,000	5.9	24
	50,000-10,000	1.2	5
	10,000-1,000	5.1	21
	<1,000	12.4	50
30-45	Total	47.3	-
	>50,000	11.7	25
	50,000-10,000	3.4	7
	10,000-1,000	-	-
	<1,000	-	-
45-60	Total	58.3	-
	>50,000	3.9	7
	50,000-10,000	13.5	23
	10,000-1,000	4.1	7
	<1,000	36.8	63
60-75	Total	71.4	-
	>50,000	2.3	3
	50,000-10,000	21.2	30
	10,000-1,000	9.6	13
	<1,000	38.3	54

VI. Core UF-VI

Date: 8-11-80
Site 1 (Piscataqua River)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
15-30	Total	44.8	-
	>50,000	12.8	29
	50,000-10,000	1.5	3
	10,000-1,000	22.5	50
	<1,000	8.0	18
30-45	Total	77.2	-
	>50,000	52.0	67
	50,000-10,000	3.3	4
	10,000-1,000	15.5	20
	<1,000	6.4	9

VII. Core UF-VII

Date: 8-11-80
Site 4 (Footman Islands)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-15	Total	34.9	-
	>50,000	4.7	13
	50,000-10,000	9.8	28
	10,000-1,000	15.3	44
	<1,000	5.1	14
15-30	Total	141.4	-
	>50,000	90.0	64
	50,000-10,000	10.9	8
	10,000-1,000	36.3	26
	<1,000	4.2	3
30-45	Total	70.1	-
	>50,000	4.7	7
	50,000-10,000	8.9	13
	10,000-1,000	38.6	55
	<1,000	17.9	25
45-60	Total	76.6	-
	>50,000	6.5	9
	50,000-10,000	9.0	12
	10,000-1,000	27.0	35
	<1,000	34.1	44
60-75	Total	123.1	-
	>50,000	51.4	42
	50,000-10,000	31.5	26
	10,000-1,000	-	-
	<1,000	-	-

VIII. Core OAX-III

Date: 4-15-81
Site 4 (Footman Islands)

Depth (cm)	Molecular Weight Range	DOC (mgC/l)	% of Total DOC
0-15	Total	16.8	-
	>50,000	3.5	21
	50,000-10,000	4.3	25
	10,000-1,000	2.2	13
	<1,000	6.8	41
15-30	Total	34.9	-
	>50,000	5.6	16
	50,000-10,000	7.8	22
	10,000-1,000	15.8	45
	<1,000	5.7	16
30-45	Total	58.9	-
	>50,000	10.7	18
	50,000-10,000	6.1	10
	10,000-1,000	33.4	57
	<1,000	8.7	15
45-60	Total	70.1	-
	>50,000	7.9	11
	50,000-10,000	11.7	17
	10,000-1,000	34.5	49
	<1,000	16.0	23
60-75	Total	75.7	-
	>50,000	8.0	11
	50,000-10,000	22.0	29
	10,000-1,000	28.9	38
	<1,000	16.8	22